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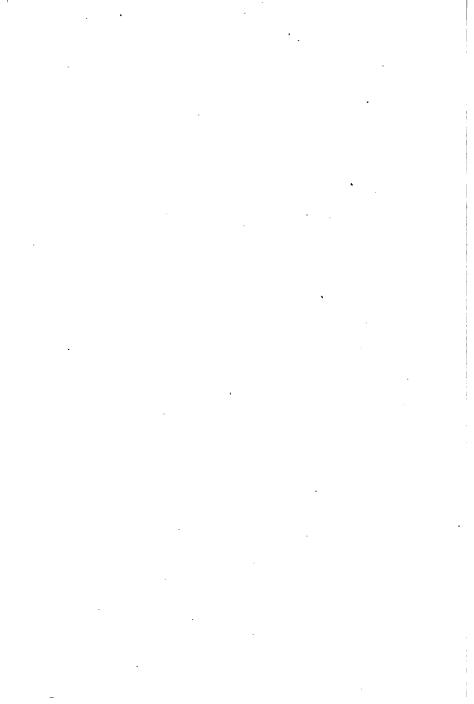
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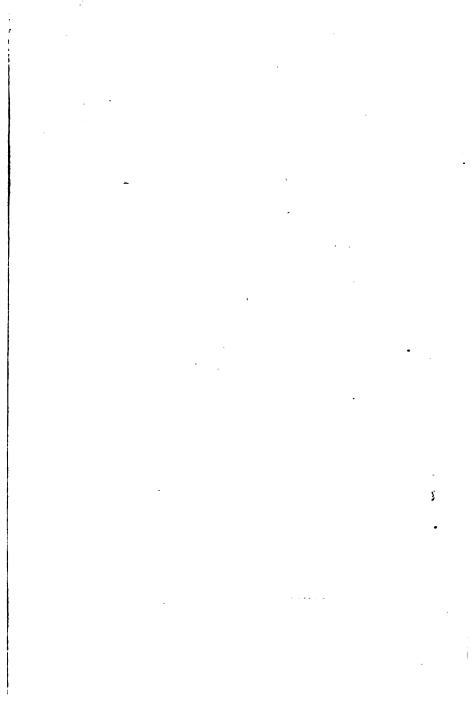
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U. S. Battleship Firing a Broadside. Many Unstable Nitrogen Compounds Decompose With Explosive Violence.

# ESSENTIALS OF MODERN CHEMISTRY

#### BY

## CHARLES E. DULL

SOUTH SIDE HIGH SCHOOL, NEWARK, N. J.



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1918

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#### PREFACE

The study of chemistry in America has been greatly stimulated by the world war. Chemical manufactures have multiplied not only to supply munitions for export but also to provide for domestic consumption certain commodities which formerly were imported. Since munition plants, with very little change, in equipment, can be used to manufacture dye-stuffs and other valuable chemicals, the chemical industries will be increasingly important after peace is restored. For these reasons the author believes there is a field for another text-book in chemistry.

The aim has been to make the book practical and to show the relation of chemistry to daily life without neglecting the fundamental principles upon which the science is based. Thus the relation of chemistry to water purification, fuels and illuminants, agriculture, paints and varnishes, textiles, paper, etc., is especially emphasized. The questions at the end of each chapter are planned to make this relationship vital.

Somewhat at variance with the usual custom, the chapters dealing with the atomic theory, equivalent and molecular weights, valence, and equations have been grouped. The treatment of these chapters is concise, and it is believed the student will gain a clear conception of the underlying principles as a whole.

It is the opinion of the author, based upon several years' experience, that the principles of metallurgy can be taught better by means of a few typical metals than by a great variety of them. Thus the reduction of iron ores with carbon is typical of the processes used in extracting many common metals. The electrolysis of bauxite illustrates another very important method of extracting metallic elements.

When the book is used with students who are not preparing for college, the chapters on the ionization theory and equilibrium may well be omitted. For such students especially, the somewhat extended discussion of the compounds of carbon will doubtless prove interesting and profitable. The entire text has been made concise enough to enable the teacher to add supplementary material for illustration.

#### Acknowledgments

The author wishes to express his thanks to all who have assisted him in the preparation of this book. He feels especially indebted to Mr. Walter J. Dumm, Barringer High School, Newark, for assistance in critical readings of the manuscript and proof; to Mr. Oscar R. Flynn, Textile Chemist, who has read all the proof and offered many valuable suggestions; to Mr. J. Edwin Sinclair, of the Central High School of Newark, for assistance in reading the proof.

The author is under especial obligation to Mr. J. C. Ware, South Side High School, Newark, for photographs from which many of the illustrations were made, and for valuable suggestions during the preparation of the manuscript. Credit for the copyrighted pictures is given in connection with the illustrations themselves.

For other illustrations, the author finds it a pleasant duty to express his thanks to the following individuals and manufacturing firms: American Water Works and Electric Co., New York; Blaugas Company of America, New York; B. D. Rising Paper Co., Housatonic, Mass.; Carborundum Co., Niagara Falls; Chilean Nitrate Propaganda, New York; Combustion Engineering Co., New York; Concrete, Detroit, Mich.; Crucible Steel Company of America, Harrison, N. J.; Demuth Glass Co., Brooklyn; Department of Works, Toronto, Canada; East Orange Public Library; Goldschmidt Thermit Co., New York; Jarecki Chemical Co., Sandusky, Ohio; Life Saving Devices Co., New York; McClure's Magazine; Newark Public Library; N. J. Experiment Station, New Brunswick; N. Y. Continental Jewell Filtration Co., Nutley, N. J.; Norton Co., Worcester, Mass.; Ox-weld Acetylene Co., Newark; Platt & Washburn Refining Co., New York; Prest-O-lite Co., Indianapolis; Radium Co., Limited, New York; Raritan Copper Works, Perth Amboy, N. J.; Scientific American; Sidio Co., New York; Standard Oil Co.; Union Sulfur Co., New York; U. S. Steel Corporation; and the Welsbach Co., Gloucester, N. J.

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# ESSENTIALS OF

# MODERN CHEMISTRY

#### CHAPTER I

#### MATTER AND ENERGY

1. Why We Should Study Chemistry.—For many reasons the study of chemistry is very important. remained for chemistry, the youngest of the sciences, to teach us the nature of such common things as the rusting of iron, the corrosion of metals, the souring of milk, the decay of foods, the action of acids on metals, and ordinary burning or combustion. For example, Plato suggested that during combustion some material escapes from the burning body, and that the heat and flames indicate the vigor with which the material rushes out. Later Stahl devised the "phlogiston" theory, in which it was assumed that "phlogiston" is present in all combustible material. In an early chapter the real nature of combustion will be studied. The introduction of the balance in modern chemistry furnished us with an explanation which is not based upon assumption, but upon facts that may be readily demonstrated by experiment.

Chemistry is not only an excellent study from an intellectual standpoint, but its importance in the industrial

world can hardly be over-estimated. By nature man is a constructive being. Before he can manufacture complex substances, however, he often finds it necessary to break them up to study their components. This work of determining "what" a substance contains, or of finding out "how much" of each constituent is present, is the sphere of the analytical chemist. For example, indigo was at one time obtained entirely from the plant kingdom. It was analyzed and its composition studied. In 1880 chemists learned how to put together its constituents, and at present the bulk of the indigo in the market is a manufactured product. Oil of wintergreen is another substance that can be manufactured at a cost much below that of extracting the natural product.

It is part of the work of the chemist to discover methods of saving and utilizing by-products. Glycerin, a by-product obtained from the manufacture of soap, is at present more valuable than the soap itself. In the manufacture of illuminating gas, coke, coal-tar, and ammonia are all valuable by-products. At one time coal-tar was considered almost worse than useless. Now scores of products are made from coal-tar and their economic value amounts to millions of dollars annually.

It has been quite truthfully said, "The civilization of a country may be estimated by the amount of sulfuric acid it uses." This statement concerning a single chemical emphasizes the relation of chemistry to the most vital questions of the present day.

2. Matter.—Anything that occupies space or takes up room is called matter. We detect its presence by the aid of one or more of the senses, as sight, smell, touch, or taste. All students recognize matter in the solid or liquid state. Every one knows that liquids occupy space, but not every one knows that gases take up room. It is impossible to pour water into a bottle filled with air or some other gas,

unless there is an opening by which the gas may escape as the liquid enters. Thus gases are included under the head of matter.

- 3. States of Matter.—There are three states of matter: solids, liquids, and gases. Solids have a definite volume and a definite shape. They do not need lateral support to maintain their form. In fact most solids are so rigid that they may be subjected to considerable pressure without distortion. Liquids have a definite volume, but they take the shape of the containing vessel. Gases have neither a definite volume nor a definite shape. They expand and fill the containing vessel. Both liquids and gases are called fluids, from the Latin word fluere, meaning to flow.
- 4. Nature of Matter and the Kinetic Theory.—From its behavior, it is quite evident that all matter is made up of very small particles, called molecules. These particles are so small that they can not be seen even with the aid of the most powerful microscope. The best estimates show that a liter of gas at standard conditions of temperature and pressure contains  $2.69 \times 10^{23}$  molecules. It is estimated that if a drop of water were magnified until it became as large as the earth, its molecules, if magnified correspondingly, would be about as big as oranges. Despite this large number of molecules, the space between the molecules is much greater than that occupied by the molecules themselves. Small as the molecules are, they are believed to be made up of atoms, very small particles that are indivisible by either physical or chemical means.

Several facts show quite conclusively that the molecules of matter are in rapid motion with respect to one another. The fact that liquids evaporate is evidence of this motion. The decided odor of naphthalene, musk, and camphor, and the rapid diffusion of illuminating gas through a room when a gas-cock is opened, furnish added proof of molecular motion

5. Measurement of Matter.—Two systems of measurement are in common use, the English system and the Metric system. The English system is probably well enough known so that it need not be discussed here.

The Metric system is a decimal system. The unit of length is the *meter*. It is divided into tenths, or *deci*-meters; into hundredths, or *centi*-meters; and into thousandths, or *milli*-meters. Ten meters make 1 *deka*-meter; 100 meters, 1 *hekto*-meter; and 1000 meters, 1 *kilo*-meter. Arranged in tabular form:

```
10 millimeters (mm.) make 1 centimeter (cm.).
10 centimeters (cm.) make 1 decimeter (dm.).
10 decimeters (dm.) make 1 meter (m.).
10 meters (m.) make 1 dekameter (Dm.).
10 dekameters (Dm.) make 1 hektometer (Hm.).
10 hektometers (Hm.) make 1 kilometer (Km.).
```

The meter equals 39.37 inches; 1 inch equals 2.54 centimeters (Fig. 1).

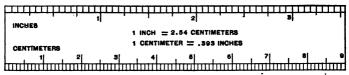


Fig. 1.—Comparison of Metric and English units of length.

The metric unit of capacity is the *liter*. The same prefixes are used as in the table of length. A cubical box 10 centimeters on a side holds 1 liter; thus it is equivalent to 1000 cubic centimeters. It is slightly smaller than the dry quart and a little larger than the *liquid* quart (Fig. 2).

The metric unit of weight is the gram. The same prefixes are used as in the table of length. One liter of distilled water at 4°C., weighs 1 kilogram. Therefore 1 cubic centimeter of water weighs 1 gram. The kilogram weight equals about 2.2 pounds; 1 ounce equals a little more than 28 grams (Fig. 3).

6. Energy.—Energy is the capacity for doing work. It requires some form of energy to produce motion in matter.

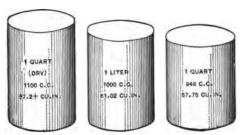


Fig. 2.—Comparison of Metric and English units of capacity.

In fact to bring about any change in the condition of matter energy is needed. In turn, changes in matter itself may liberate various forms of energy.

7. Kinds of Energy.—There are several kinds of energy: mechanical energy; heat energy; electrical energy; light energy;

and chemical energy. For doing chemical work all of the above-named are used extensively. Energy can not be destroyed. It is possible to convert or transform one kind of energy into a different form. Thus it is possible to use heat energy from





Fig. 3.—Comparison of Metric and English units of weight.

burning coal to produce steam; the steam may be used in a steam-engine to furnish mechanical energy; electrical energy may be generated by a dynamo turned by such mechanical energy; and electrical energy may in turn be easily transformed into heat, light, or mechanical energy.

?

#### SUMMARY

Chemistry is a cultural study since it answers many important questions. It is intensely practical, since it is so important a factor in manufacturing and industrial operations.

Matter is anything that occupies space.

There are three states of matter: solids, liquids, and gases.

According to the kinetic theory, matter is made up of molecules; these molecules are in very rapid motion.

The Metric system is used extensively in scientific work. The meter is the unit of length; the liter, the unit of capacity; and the gram, the unit of weight. In the laboratory solids are usually measured by weight; gases by volume; and liquids by either volume or weight.

Energy is the capacity for doing work. There are several kinds of energy: mechanical, heat, light, electrical, and chemical energy.

#### **PROBLEMS**

- 1. Find the number of grams in a pound. Find your weight in kilograms.
- 2. Reduce your height to meters. Find the value of 10 Km. in miles.
- 3. What must be the dimensions in decimeters of a cubical box whose capacity is 1 liter? How many cubic centimeters are there in 22.4 liters?
- 4. What advantages has the Metric system over the English system?
- 5. A pneumatic trough is 30 cm. long, 2 dm. wide, and 80 mm. deep. What is its capacity in cubic centimeters? In liters?
- 6. A bottle holds 1650 c.c. How many grams of water does it hold? How many liters? How many kilograms?
- 7. A test-tube 6 in. long has an internal diameter of ¾ in. How many cubic centimeters does it hold?

Topic for Reference.—History of the Metric System. See Appendix C.

#### CHAPTER II

#### ELEMENTS—MIXTURES—COMPOUNDS

- 8. Classes of Substances.—Substances may be classified as elements, mixtures, and compounds. The number of elements known is not very great, but the number of mixtures and compounds is enormous. When the various elements are studied in chemistry, the more important compounds formed by them are usually discussed at the same time as a matter of convenience and for purposes of classification.
- 9. The Element is the Limit of Analysis.—In the preceding paragraph we learned that the number of complex substances is very great. The analysis of a complex substance, or of a chemical compound, consists in separating it into simpler substances. We soon reach a point, however, where the constituents do not yield to further sub-division. For example, if we heat the red powder known as mercuric oxid, it decomposes readily, yielding two substances, mercury and oxygen. All attempts to decompose either mercury or oxygen into still simpler substances have resulted in failure. For that reason they are called elementary substances, or elements.

It is quite impossible to prove that any given substance is an element. We know that no one has yet succeeded in decomposing oxygen into simpler substances, but we can not prove that some one will not succeed in doing so in the future by the use of some as yet untried method. At one time water was considered an element, but it has since been decomposed into hydrogen and oxygen, two simpler substances.

10. Number and Distribution of the Elements.—At the present time slightly more than eighty substances are known that chemists have good reason to believe are elements. New ones are being discovered from time to time. Such substances as iron, copper, oxygen, nitrogen, lead, silver, and gold have been tested in almost every conceivable manner without their decomposition into other substances. Of the eighty-odd elements known, not more than half are well known. Even the names of many elements are not familiar, even to well-educated persons. The student will be interested in comparing the list of fairly common elements given on page 9 with the complete list given on the back cover.

According to an estimate made by Clarke, about 98 per cent. of the earth's crust is composed of eight elements in about the following proportion:

	Per cent.
Oxygen	. 47.0
Silicon	. 28.0
Aluminum	. 7.9
Iron	. 4.4
Calcium	. 3.4
Magnesium	. 2.4
Sodium	. 2.4
Potassium	. 2.4

11. Names and Symbols.—Metals recently discovered have the Latinized ending "um" or "ium," as sodium, calcium, potassium, radium, and aluminum. The stem used may depend upon some characteristic property of the element, the source from which it is obtained, or it may be the name of the country in which the element was discovered.

For convenience, symbols are used to designate elements. They serve as abbreviations, but the student will learn later that a symbol means more than an abbreviation. For example, the letter O is used to represent oxygen; it also means one atom of oxygen, or the smallest particle of oxygen that can enter into combination with other elements. Usually the first letter of the name of an element is used as its symbol, as H for hydrogen, N for nitrogen, or C for carbon. When the names of several elements begin with the same letter, some other letter is used with the initial letter, as Cl for chlorin, Ca for calcium, and Cr for In several cases the symbol is derived from the chromium. Latin name for the element. Thus Fe from the Latin word ferrum is the symbol for iron; Pb from the Latin word plumbum is the symbol for lead; and Na from natrium is the symbol for sodium. The following table gives the names and symbols of the most common elements.

(The following table is for reference only.)

AluminumAl	LeadPb
AntimonySb	LithiumLi
ArgonA	MagnesiumMg
ArsenicAs	ManganeseMn
BariumBa	MercuryHg
BismuthBi	NickelNi
BoronB	NitrogenN
Bromin Br	OxygenO
CadmiumCd	PhosphorusP
CalciumCa	PlatinumPt
CarbonC	PotassiumK
ChlorinCl	Radium Ra
Chromium Cr	SiliconSi
CobaltCo	SilverAg
CopperCu	SodiumNa
FluorinF	StrontiumSr
GoldAu	SulfurS
HydrogenH	TinSn
IodinI	TungstenW
IronFe	ZincZn

- 12. Metals and Non-metals.—Elements are divided into two classes, metals and non-metals. Substances that have a luster like steel, that conduct heat and electricity fairly well, are called metals; substances like sulfur and phosphorus, that have a glassy or waxy luster, and are poor conductors of heat and electricity, are classed as non-metals. This classification is an old one that is still retained, although it is not strictly correct. The division line is not sharply defined, since such elements as arsenic and antimony, being on the border line, have some metallic and some non-metallic properties. Such elements are sometimes called metalloids.
- 13. Mixtures and Compounds.—When a substance is made up of two or more elements, they may be mechanically mixed, or they may be chemically combined. The following experiment serves to show the differences between a mixture and a compound. If we put a few iron filings on a piece of paper and add to them a little powdered sulfur, there is no apparent action between them. No heat is gained or lost, no light is emitted, and there is no evidence that electricity is produced. The two elements may be mixed in any proportion. If we pass a magnet over the mixture the iron filings are attracted to it and may be readily separated from the sulfur. If we put the mixture in a test-tube and heat it slightly, a vigorous action takes place. The contents of the tube begin to glow, and even if the external heat is withdrawn, the whole mass soon becomes red hot. Subsequent examination of the product formed shows that an entirely new substance with different properties than either the iron or the sulfur possessed has been formed. be decomposed by mechanical means. If the ingredients had been weighed, the results would have shown that 7 parts by weight of iron always combine with 4 parts by weight of sulfur. Any excess of either element is always left uncombined.

Air, flour, baking powder, and the various kinds of soils are examples of mixtures. The per cent. of their constituents may vary widely. Water, starch, sugar, and salt are examples of compounds. Their constituents are always present in the same proportion by weight. The several differences between a mixture and a compound may be summarized in the following contrasting table:

#### MIXTURE

In a mixture the constituents may be present in any proportion.

In preparing a mixture, there is no evidence of any chemical action, such as the evolution of heat, light, gas, or electricity.

A mixture may often be separated by mechanical means.

#### COMPOUND

A compound always has a definite composition by weight.

In the preparation of a compound, some evidence of chemical action is apparent. Heat or light may be emitted or absorbed, an electric current produced, or a gas liberated.

The constituents of a compound can be isolated by chemical means only.

- 14. Law of Definite Proportions.—John Dalton was the first to call attention to the chief difference between a mixture and a compound. This difference is clearly formulated in Dalton's law of definite composition or proportion: Every compound has a definite composition by weight. This is the fundamental law upon which the whole science of modern chemistry is based.
- 15. Formulas.—A formula is often used to show of what constituents a compound is made up. The formula for water is H<sub>2</sub>O. This formula represents 1 molecule of water. It shows that each molecule of water contains 2 atoms of hydrogen and 1 atom of oxygen. If we write 2H<sub>2</sub>O, the expression represents 2 molecules of water, each containing 2 hydrogen atoms and 1 oxygen atom. The number before a formula always shows the number of

molecules taken; the number following each symbol shows the number of atoms of that element in each molecule of that compound.

16. Properties of Elements and Compounds.—We identify elements and compounds by means of their properties. There are certain general properties common to all matter. Of course such properties are of no value for identification purposes. However, all substances have certain special properties by means of which we recognize them. The more peculiar the properties of a substance, the easier it is to identify it. Alcohol is easily recognized by its peculiar odor. Ammonia may be detected by its odor. Table salt may be identified by its taste. Since the number of compounds that may be formed from the elements is almost infinite, the only method suitable for the chemist is to classify compounds according to similar properties, and then identify each one by its peculiar individual properties.

In studying properties we distinguish between physical properties and chemical properties. Under physical properties are included color, odor, taste, solubility in water, hardness, density, conductivity of heat and electricity, tenacity, ductility, and malleability. Under chemical properties we include all chemical activity such as the interaction of the substance with water, air, acids, and alkalis.

#### SUMMARY

Substances are classed as elements, mixtures, and compounds. An element is a substance that no one has succeeded in decomposing into simpler substances. More than eighty elements are known. About half of these are common. It is estimated that more than 98 per cent. of the earth's crust is made up of only eight elements. Elements are classed as metals and non-metals.

Symbols are used to represent elements. The symbol is usually the first letter of the name of the element or the first letter and some other letter whose sound is conspicuous as the name of the element is pronounced.

A substance made up of two or more elements is either a mixture or a compound. If the elements are chemically combined and their proportion definite, the substance is a compound. In a mixture the constituents may be in any proportion.

A formula is a group of symbols used to show the composition of a compound. It also shows the number of atoms in each molecule of that compound.

Elements and compounds are identified by means of certain special properties. Such properties are either physical or chemical.

#### **OUESTIONS**

- 1. Name five elements; four compounds; three mixtures.
- 2. If you were given a mixture of sand and sugar, how could you separate them?
- 3. How could you separate the iron from a mixture of iron filings and sulfur?
- 4. State some of the characteristic properties of (a) gasoline, (b) alcohol, (c) gold, (d) copper, (e) silver.
- 5. How would you distinguish between alcohol and gasoline? How would you tell gold from copper? Salt from sugar?

#### CHAPTER III

#### CHANGES IN MATTER

17. Physical and Chemical Changes.—Changes in matter are of two kinds, physical and chemical. In a physical change the matter does not lose its characteristic properties. Its form or its state may be changed. The melting of ice, changing water to steam, breaking glass or wood, and dissolving salt in water are all examples of physical change. In none of these cases does the substance lose its identity; the molecule is not broken up.

In a chemical change, the substance loses its identity and forms a new substance or substances with new properties. Molecules are made up of small parts called atoms. During a chemical change, the molecule may be decomposed, its atoms may be re-arranged, or a more complex molecule may be built up by putting together certain elements. The burning of wood, the action of an acid on metals, the decay of plants, and the cooking of meat and eggs are all examples of chemical change.

18. Causes of Chemical Change.—Heat, light, electricity, and solution are the most common causes of chemical change.

Wood does not begin to burn until it is heated strongly; the head of a match is ignited by the heat produced by friction; heat causes the chemical change in the baking of bread and the cooking of foods. In the laboratory heat is generally applied to bring about a chemical change. Heat is also used to increase the speed of a chemical reaction. It has been determined that the speed at which

a chemical reaction proceeds is practically doubled by increasing the temperature 10°C.

Every one knows that certain colors fade in sunlight. The student knows that a photographic plate is affected when exposed to the light. Plants need sunlight for making starch out of the raw materials obtained from the air and soil. A plant kept in the dark soon loses its green color and becomes unable to manufacture its food. These are all examples of the action of light in producing chemical change. The fact that many chemicals, such as hydrogen peroxid, are kept in dark-colored bottles is further indication that light is a very active agent in producing chemical changes.

When an electric current is passed through water to which a few drops of sulfuric acid have been added, decomposition occurs and the elements hydrogen and oxygen are liberated. Many compounds, when melted, or dissolved in water, may be separated into their elements by the passage of an electric current through the molten mass, or the water solution. Electricity is used commercially in the refining of metals, in electroplating, and in electrotyping.

Many substances that show no chemical action when they are mixed in the dry state, interact readily when in solution. Baking powder is a mixture of compounds that remains unchanged if kept dry; as soon as water is added, a chemical change occurs. Light causes a chemical change in making blue-prints. The blue-prints are developed by the addition of water, which causes a second chemical change.

19. Classes of Chemical Change.—There are four classes of chemical change: analysis, or decomposition; synthesis, or composition; substitution; and metathesis, or double substitution.

Analysis is the separation of a compound into its elements. When an electric current is passed through water as above, the compound is broken up into its elements. Heating mercuric oxid decomposes it into mercury and oxygen. The word equation,

water 
$$\rightarrow$$
 hydrogen + oxygen,

is read as follows: water forms (when decomposed) hydrogen and oxygen. In all chemical equations the arrow is read "forms," "gives," or "produces." The plus sign is usually read "and." The equation,

mercuric oxid → mercury + oxygen,

is read as follows: mercuric oxid (when heated) "produces" mercury and oxygen.

Synthesis is the building up of a compound by the direct union of its elements. By mixing hydrogen and oxygen and passing an electric spark through the mixture, the compound, water, may be formed. The equation, hydrogen + oxygen - water, is just the reverse of the equation shown under analysis. It often happens in chemistry that a different agent or different treatment may cause a complete reversal in the direction of a chemical reaction. To show that a reaction is reversible, two arrows, pointing in opposite directions, are often used. For example, the double arrow in the equation,

shows that under certain conditions water may be formed by the union of its elements, and that under other conditions water decomposes, yielding hydrogen and oxygen. If we rub together in a mortar a globule of mercury and a crystal of iodin, they combine to form mercuric iodid. The equation is as follows:

mercury + iodin → mercuric iodid.

In substitution one element may take the place of another, or be substituted for it. For example, if we suspend a strip of zinc in a solution of some lead salt, the zinc goes into

solution and metallic lead is formed as represented by the following equation,

 $zinc + lead solution \rightarrow zinc solution + lead.$ 

An arrow pointing upward indicates that the product is gaseous; a downward pointing arrow indicates that the product is a precipitate, or an insoluble substance.

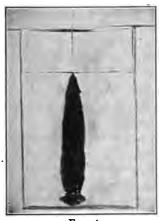


Fig. 4a

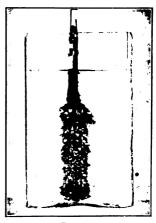


Fig. 4b.

Fig. 4a.—The zinc strip goes into solution, replacing the lead which is deposited in the form of crystals.

Fig. 4b.—The zinc goes into solution, replacing the tin. (Substitution.)

In metathesis there is a double substitution; it is really a change of partners. If we mix solutions of sodium chlorid and silver nitrate, the sodium and silver exchange places. The word equation, sodium chlorid + silver nitrate  $\rightarrow$  silver chlorid + sodium nitrate, shows clearly what occurs during the chemical change.

20. Energy Involved in Chemical Changes.—Although heat is often needed to start a chemical reaction, yet heat energy is often produced as the action proceeds. For

example, external heat is used to enkindle wood or coal, but heat is liberated continuously as the fire burns.

A chemical reaction that liberates heat as it progresses is said to be exothermic.

A reaction that absorbs heat during its progress is said to be *endothermic*. Unless external heat be applied constantly, the action stops.

Other forms of energy are often attendant upon chemical change. Light energy may be evolved, or it may be used to produce the change. Electricity is often produced as a chemical reaction occurs. In a voltaic cell the negative plate is acted upon chemically and the chemical energy is transformed into electrical energy. Even mechanical energy may be liberated during chemical action, as in the detonation of such substances as nitro-glycerin and dynamite, or in the explosion of gun powder.

- 21. Distinction Between Physics and Chemistry.—
  Physics may be defined as the science that deals with physical changes. The molecule is the physical unit; so long as it remains intact, we are dealing with physics, and any change in matter is physical. Chemistry is the science that deals with chemical changes; it includes also a study of elements and compounds. In the study of chemistry the atom is the unit. The chemist builds up compounds from atoms. He sometimes decomposes compounds into simpler compounds or into their elements.
- 22. Inter-relation Between Physics and Chemistry.—
  Physics and chemistry are very closely related. We have seen that heat, light, and electricity, all forms of energy studied in physics, are the chief factors producing chemical changes. We have also seen that chemical energy may be transformed into heat, light, or electricity. In chemistry we study both the physical and chemical properties of elements and compounds. A change in temperature or atmospheric pressure very often changes the

nature of a chemical reaction. Because these two sciences are so closely related, much attention is given to the courses in physical chemistry as offered by our universities.

#### SUMMARY

Changes in matter are physical or chemical; in a physical change the characteristic properties of the substance are not lost; in a chemical change a new substance with new properties is formed.

Heat, light, electricity, and solution are the chief causes of chemical change.

Chemical changes are of four classes: analysis, synthesis, substitution, and metathesis.

When heat is liberated during a chemical change, the reaction is said to be exothermic; when heat is absorbed during the change, we have an example of an endothermic reaction.

Physics deals with physical changes; chemistry deals with chemical changes and the study of elements and compounds.

It often happens that a physical cause produces a chemical effect or at least so affects the efficiency that a study of physics is very important to a clear understanding of chemistry.

#### QUESTIONS

- 1. State whether the following changes are chemical or physical:
- (a) The burning of wood.
- (b) The souring of milk.(d) Weaving cotton cloth.
- (c) The fermentation of sugar.(e) The decay of food.
- (f) Melting of lard.
- (g) Tarnishing of brass.
- (h) Rusting of iron.
- (i) The evaporation of alcohol.
  - (j) The explosion of dynamite.
- 2. Formerly it was customary to mix soda and sour milk directly when used for baking; now it is customary to mix the soda with the flour and then add the sour milk. Is there a good reason for the latter practice?
  - 3. Which of the chemical changes of question 1 are exothermic?

#### CHAPTER IV

#### OXYGEN

- 23. Occurrence.—We have already learned that oxygen is the most abundant element. Most common substances contain a high percentage of oxygen. Water is more than 88 per cent. oxygen; clay, sand, and limestone are about 50 per cent. oxygen; and the air itself is rather more than 20 per cent. oxygen. It is also present in all plant and animal tissues.
- 24. Preparation.—There are many ways of preparing oxygen. Only three will be given here:
- 1. By Heating Mercuric Oxid (Historical).—Mercuric oxid is a red powder composed of mercury and oxygen. When this powder is heated strongly the oxygen is given off and mercury remains. This is an expensive method of preparing oxygen and is of interest from its historical value only. In 1774 Priestley prepared oxygen by heating this red powder. Priestley did not name the gas oxygen. He described it as a gas having about the same properties as air, but in "greater perfection."

Scheele, a Swedish chemist, working independently discovered oxygen at about the same time, but his results were not published until 1777.

2. By Heating a Mixture of Manganese Dioxid and Potassium Chlorate (Usual laboratory method).—Potassium chlorate is a white crystalline solid consisting of potassium, chlorin, and oxygen. About 39 per cent. by weight is oxygen. When this compound is heated, either alone or mixed with manganese dioxid, oxygen is liberated. The

gas is collected by water displacement as shown in Fig. 5. The following word equation shows how decomposition occurs:

potassium chlorate -- potassium chlorid + oxygen.

potassium | potassium chlorin | chlorin oxygen

The manganese dioxid serves here as a catalytic agent. When it is present the decomposition of the chlorate proceeds more rapidly, the evolution of the gas is more regular

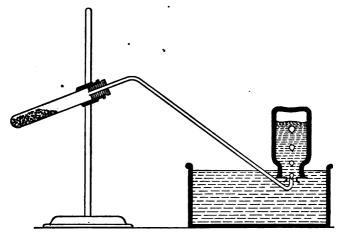


Fig. 5.—Apparatus for preparing oxygen.

and it occurs at a lower temperature. The manganese dioxid appears unchanged at the end of the reaction. Any substance which by its presence aids in producing or accelerating chemical action without itself being permanently changed is called a catalytic agent. It is similar to the action of a whip on a horse; without helping the horse it makes him go faster. There are also cases of negative catalysis. For example, acetanilid is added to hydrogen peroxid to prevent or retard its decomposition.

3. By Electrolysis (Commercial).—When a current of electricity is passed through acidulated water, oxygen is liberated at the positive terminal and hydrogen at the negative terminal (Fig. 6). This method is used for preparing oxygen on a large scale for commercial use. It is

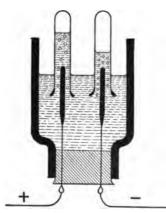


Fig. 6.—Apparatus for the electrolysis of water.

forced into steel cylinders under pressure and put on the market in that form.

25. Physical Properties.—Pure oxygen is a colorless, odorless, tasteless gas. It is slightly heavier than air. At standard conditions of temperature and pressure (0°C. and a pressure of 1 atmosphere or 760 mm. of mercury), 1 liter of oxygen weighs almost 1.43 grams. One liter of air at the same standard temperature and pressure weighs about 1.29 grams. It is

slightly soluble in water, 3 volumes of oxygen dissolving in 100 volumes of water at the ordinary temperature. If a glass of water stands for some time in a warm room, bubbles of gas appear. This is largely oxygen, which is less soluble in warm water than in cold. Like all gases, if cooled sufficiently while the pressure upon it is increased, it is converted into a liquid. Liquid oxygen is pale blue in color.

26. Chemical Properties.—The most important chemical property of oxygen is its activity. At ordinary temperatures oxygen interacts slowly with substances or in some cases not at all. At higher temperatures it reacts rapidly with most substances, usually with the evolution of heat and light.



Antoine Laurent Lavoisier (1743-1794), a French investigator, is called the founder of modern chemistry. By the use of the balance he proved that whatever the change in matter, the total amount remains the same. He studied combustion and showed that mercury gains in weight when heated in the air. He explained the composition of air and water. gave to hydrogen and oxygen their present names, and advocated the theory of the indestructibility of matter.

Joseph Priestley (1733-1804), an English writer, is generally considered the discoverer of oxygen. He collected gases by mercury displacement, and invented the pneumatic trough. He discovered ammonia, nitrous oxid, and nitric oxid. Priestley was a stanch supporter of the phlogiston theory of combustion. He believed the gas hydrogen to be phlogiston.





27. Oxidation.—That process by which oxygen unites with some other substance is called oxidation. It may occur slowly, in which case it is not generally accompanied by light or noticeable heat, or it may occur rapidly. The rusting of some metals, and the decay of wood and vegetable matter are examples of slow oxidation.

The oxygen may be furnished by the air or by some substance rich in oxygen. Any compound that gives up its oxygen to a substance more readily than the air is a good oxidizing agent. Potassium chlorate is an example.

The compound formed by the union of oxygen with some other element is called an oxid. In chemistry a binary compound, or one containing only two elements has the ending id.



Fig. 7.—A burning oil-tank. The combustion is so rapid that only a part of the carbon is oxidized.

28. Combustion.—Any chemical action that occurs so rapidly that light and heat are produced, is called combustion. Ordinary burning is rapid oxidation (Fig. 7). The nature of ordinary combustion was first shown by Lavoisier, a French Chemist.

He had been studying the rusting of metals in air, and, hearing of Priestley's experiments, he concluded that the "perfect air" described by him was only a very active part of ordinary air. Using an apparatus like that shown in Fig. 8, he heated a weighed quantity of mercury in the retort r. The bell-glass b contained a definite volume of air confined by the mercury in the dish d. During the heating the mercury in the dish rose in the bell-glass showing that the volume of air was being diminished. At the same time the mercury was being converted into a red powder.

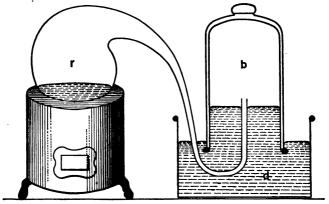


Fig. 8.—Apparatus illustrating method used by Lavoisier to show the nature of combustion.

After 12 days the action stopped. The mercury in the retort had increased in weight and the volume of air in the bell-glass had shrunk to about four-fifths its original volume. Evidently one-fifth of the air had united with the mercury to form the red powder. When this powder was afterward heated more strongly, a gas was given off which was like Priestley's "perfect air."

Lavoisier named this gas oxygen and proved by his experiment that ordinary burning is the union of oxygen with some other substance. Due to this discovery, Lavoisier is commonly called the father of modern chemistry.

Since only about one-fifth of the air is oxygen, substances

burn more rapidly in oxygen than in air and some substances burn readily in oxygen that do not burn in air. A glowing splinter thrust into a bottle of oxygen bursts into flame. This serves as a test for oxygen. Iron burns in oxygen giving off dazzling white sparks.

Since oxygen is required for ordinary burning, the gas is said to support combustion.

# 29. Kindling Temperature.

—The furniture of a room is



Fig. 9.—Match (longitudinal section).

surrounded by air containing oxygen, but it does not take fire. Before wood begins to burn, heat must be applied to raise it to a certain temperature. The temperature at which a substance takes fire, or begins to burn, is called its kindling temperature. This temperature varies with the nature of



Fig. 10.—Match head in flame shows that combustion occurs at the surface only.

the substance. Phosphorus has a very low kindling temperature, a slight amount of friction raising its temperature enough to enkindle it. The head of a match is made of some material that has a low kindling temperature. As it burns the reaction is exothermic, and enough heat is liberated to enkindle the match-stick (Fig. 9).

Since in burning, the oxygen unites with the substance, combustion can occur at the surface only. A match supported as in Fig. 10 in the center of the flame of a Bunsen burner is not enkindled, showing that such a flame is hollow and

that combustion occurs at the surface only. This fact may also be shown by momentarily thrusting a sheet of paper down upon the flame. The charred spot on the paper will be circular. It will be of interest to study the effect of increasing the surface of a combustible substance. If 28 OXYGEN

we split a block of wood, two new surfaces are exposed to the oxygen and combustion is more rapid. If these pieces are split again still more surface is exposed. A powdered substance has such an extensive surface that it burns almost instantly, or explosively if it is loose enough so oxygen can penetrate it readily. One type of explosion may be defined as practically instantaneous combustion throughout the entire mass.

- 30. Principles Involved in Extinguishing Fires.-We have seen that three things are necessary for combustion to occur: (1) Combustible material; (2) a supply of oxygen; (3) the substance must be raised to its kindling temperature. Extinguishing a fire may be accomplished: (1) by removing the combustible material; (2) by shutting off the supply of oxygen; (3) by cooling the substance below its kindling temperature. The successful application of any one of these principles extinguishes the fire. In large city fires, buildings are often dynamited to make the combustible material inaccessible. Water lowers the temperature and as it evaporates, its vapor shuts off the supply of oxygen. A wet blanket, or a quantity of sand, shuts off the oxygen supply. The effect of lowering the temperature may be seen by holding a copper spiral in a candle flame. The copper conducts the heat away so rapidly that the temperature falls below the kindling point.
- 31. Spontaneous Combustion.—Several substances oxidize slowly even at the ordinary temperature and some heat is produced. If the air can not circulate freely to disseminate the heat, or if the substance is a very poor conductor, the accumulation of heat may eventually raise the temperature to the kindling point. Oily rags thrown in a closet and left undisturbed are a source of danger since the slow oxidation of the oil may heat them to their kindling temperature. Fires are often started in this way by spontaneous combustion.

- 32. Products of Combustion.—Illuminating gas contains compounds of carbon and hydrogen. As it burns the carbon unites with the oxygen to form carbon dioxid. The hydrogen unites with oxygen forming water. If a beaker of cold water is held in the flame of a Bunsen burner, drops of water formed from the burning hydrogen soon condense on it. The wax of a candle is also composed of carbon and hydrogen. If a short piece of candle is put in a wide-mouthed bottle and lighted; it soon goes out after the bottle is stoppered, the oxygen being used up. A little limewater poured into the bottle becomes milky as the bottle is shaken showing that carbon dioxid was formed by the burning candle. Wood and coal also form water and carbon dioxid when burned. The mineral matter remains as an ash. Thus the chief products of ordinary burning are water and carbon dioxid.
- 33. Weight Changes in Burning.—Lavoisier found that mercury increases in weight when it is converted into the red powder, mercuric oxid. The same is true of all metals that unite with oxygen, such as magnesium, tin, copper, and iron. The increase in weight is evidently due to the weight of the oxygen added.

Wood and coal appear to lose weight when burned. If, however, we weigh both the ash that remains and the gases that are produced, we find that in these cases also there is a decided increase in weight. One ton of pure charcoal forms about  $3\frac{2}{3}$  tons of carbon dioxid when it burns.

34. Incombustible Material.—It is easy to see why water does not burn if we stop to consider that the hydrogen it contains has already united with all the oxygen it can hold. The same is true with carbon dioxid. Many substances that do not burn are oxids similar in nature to these products of combustion, water and carbon dioxid. For these reasons such substances as magnesium oxid and calcium oxid make good fireproof materials.

35. Relation of Oxygen to Life.—Oxygen is one of the most important elements. Without it animals could live only a short time. Taken in through the lungs, it is carried by the hemoglobin of the blood to all parts of the body. It oxidizes a part of the food, thus supplying warmth to



Fig. 11.—Self-contained oxygen breathing apparatus.

the body and furnishing it with heat energy. It oxidizes the waste tissues so they may be readily removed by the organs of excretion. Carbon dioxid and water vapor, waste products from oxidation are exhaled from the lungs.

36. Decay.—Plant and animal tissues contain carbon and hydrogen. Decay is the slow oxidation of The presthese tissues. ence of bacteria is necessarv before decay can occur. For this reason dry wood does not decay since bacteria grow on moist substances only. The spoiling of food is often due to slow oxidation in the presence of bacteria.

37. Uses of Oxygen.—It is possible to buy oxygen kept in metal cylinders under considerable pressure. It finds extensive use with hydrogen in the oxy-hydrogen blowpipe or with acetylene in the oxy-acetylene blowpipe. The very high temperature produced as these gases under pressure are burned makes the flame suitable for melting, cutting, or welding metals.

Oxygen helmets are used extensively by firemen and miners whose work makes it necessary for them sometimes to enter buildings or mines filled with smoke or poisonous gases. The oxygen is generated by chemicals and supplied through a flexible tube to a mask that fits over the nose and mouth of the wearer, or in some cases it is supplied from small storage cylinders. Fig 11 shows a self-contained oxygen-breathing apparatus. Oxygen under pressure is



Fig. 12.—The lungmotor is a double action pump used for artificial respiration. The piston stroke may be adjusted to vary the capacity.

carried in cylinders at the back. Through a reducing valve it is supplied to the breathing bag which is carried on the wearer's chest.

Pure oxygen is often given to persons suffering from pneumonia or in case the person is too weak to inhale the necessary volume of air. In case of asphyxiation from inhaling smoke, illuminating gas, or from electric shock, a pulmotor or a lungmotor is used. By means of the lung32 OXYGEN

motor air rich in oxygen is pumped into the lungs at about the same intervals as in ordinary breathing. In some cases pure oxygen is used (see Fig. 12).

Oxygen in the air itself is a very valuable aid in destroying bacteria. Rivers containing sewage are purified in flowing considerable distances by contact with the oxygen in the air. In some sewage disposal plants the sewage is sprayed into the air to be purified by the oxygen. A similar method is used for purifying city water supplies.

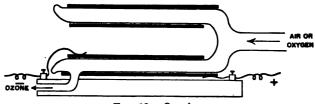


Fig. 13.—Ozonizer.

38. Ozone.—It is not unusual for the same element to exist in two or more different forms. Each is called an allotropic modification of the other. Ozone is an allotropic form of oxygen.

Ozone is prepared commercially by passing the "brush discharge" of an electrical machine through oxygen. Fig. 13 shows an ozonizer. The tin foil layers on the inner and outer tube are connected to the terminals of an induction coil. A current of air or oxygen passes slowly through the space between the concentric tubes.

Ozone has an irritating odor. It is heavier than oxygen and considerably more soluble in water. It is much more active at the ordinary temperature than oxygen. It attacks silver and mercury forming black oxids of these metals. Bacteria are readily destroyed by ozone. It is one of the most vigorous oxidizing agents known. It causes many colors to fade very rapidly. At a high temperature it is converted into oxygen.

Ozonizers have been recently installed in connection with ventilating systems to free the air from bacteria. Their usefulness in this respect is still a debatable question. In several cities, as Lille, Paris, and Petrograd, ozone is used to purify water in city reservoirs. Ozone is also coming into fairly extensive use in the bleaching industry. In both cases it has the advantage over other bleaching and disinfecting agents of leaving no injurious products after the action is complete, since only oxygen remains.

#### SUMMARY

Oxygen is prepared commercially by the electrolysis of water. In the laboratory it is usually prepared by heating a mixture of potassium chlorate and manganese dioxid.

Oxygen is a colorless, odorless, tasteless gas. It is slightly soluble in water. One liter of oxygen weighs 1.43 grams. Chemically oxygen is among the most active elements, especially at high temperatures.

A catalytic agent is a substance that aids chemical action without itself being permanently changed.

The process by which oxygen unites with some other substance is called oxidation. The compound furnishing the oxygen is the oxidizing agent. The substance upon which the oxygen acts is oxidized. The product formed is usually an oxid.

Ordinary combustion is rapid oxidation. Before a substance unites with oxygen so rapidly that light and heat are produced it must be heated to a point called its kindling temperature.

Three things are needed for combustion: (1) combustible material; (2) a supply of oxygen; (3) the material must be heated to its kindling temperature. Fires are extinguished by eliminating any one of the above factors.

Substances increase in weight when burned on account of the addition of oxygen.

Water and carbon dioxid are products of ordinary combustion.

Ozone is a very active form of oxygen.

## **QUESTIONS**

- 1. Why would fishes die if put in an aquarium of water which had been heated to the boiling point and subsequently cooled?
- 2. What changes would occur in nature if the air were pure oxygen?
- 3. What products are formed by burning tin, copper, phosphorus, magnesium, iron, and sulfur?
- 4. In starting a hard coal fire, paper, wood, and coal are usually added successively. Explain.
- 5. When one end of a splinter is thrust into a flame, why does it not burn throughout its entire length as soon as it is enkindled?
- 6. Why are manufacturers especially interested in catalytic agents?
  - 7. Why does a book or magazine burn so slowly?
- 8. Why is a candle extinguished by blowing? Why does blowing a fire cause it to burn more vigorously?
- 9. Since powdering a substance makes it burn more rapidly, why is it so difficult to burn coal dust in a furnace?
- 10. Which should you use to put out a gasoline fire, water or sand? Why?
- 11. Baking soda gives off carbon dioxid when heated. Is it suitable for use in fire extinguishers?
- 12. Pyrene fire extinguishers contain carbon tetrachlorid, a volatile liquid whose vapor does not burn. Explain how it puts out a fire.
- 13. If water is 88.88 per cent. oxygen, how many liters of oxygen can be prepared from 100 grams of water by electrolysis?
- 14. How many liters of oxygen can be obtained from 5 grams of potassium chlorate, if it is 39 per cent. oxygen?

Topics for Reference.—The Davy safety lamp. Brin's process for making oxygen. Construction of the oxygen helmet. Phlogiston. Theories of the Alchemists.

#### CHAPTER V

## HYDROGEN

- 39. Occurrence.—Although not an abundant element, yet hydrogen is widely distributed. Since it is present in all plant and animal tissues it is a very important element. Water is one-ninth hydrogen; all acids contain hydrogen.
- 40. Preparation.—There are several ways of preparing hydrogen, of which three are given here.
- 1. By the Electrolysis of Water (Commercial).—Under oxygen we learned that water may be decomposed by passing an electric current through it. The gas that appears at the positive terminal is oxygen; that which is collected at the negative terminal is hydrogen. The hydrogen thus obtained is stored in steel cylinders under pressure.
- 2. By Substituting a Metal for the Hydrogen in Water.—Some very active metals, such as sodium and potassium, decompose water liberating a part of its hydrogen, and combining with the oxygen and part of the hydrogen. Enough heat is liberated to melt the metal, which floats on the surface of the water. Potassium furnishes enough heat to enkindle the hydrogen. That the action is one of substitution may be seen from the following word equation:

$$\begin{array}{c} \text{Sodium} + \text{water} \rightarrow \text{hydrogen} + \text{sodium hydroxid} \\ \text{ } \left\{ \begin{array}{c} \text{hydrogen} \\ \text{oxygen} \end{array} \right. \\ \end{array} \\ \begin{array}{c} \text{sodium} \\ \text{hydrogen} \\ \end{array}$$

The sodium hydroxid is a white caustic solid that may be obtained by evaporating the undecomposed water.

Magnesium decomposes boiling water slowly. Iron is another metal that decomposes water at a high temperature. When steam is passed over heated iron the oxygen of the steam unites with the iron and hydrogen is set free, according to the following equation:

3. The Action of Acids on Metals (Usual laboratory method).—All acids contain hydrogen. Many metals

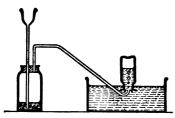


Fig. 14.—Hydrogen generator.

Metals (Usual laboratory hydrogen. Many metals interact with acids in water solution, setting free their hydrogen. Zinc or iron is usually used with dilute sulfuric acid or dilute hydrochloric acid. Fig. 14 shows the apparatus commonly used in the laboratory to prepare hydrogen.

The gas is collected by water displacement. The speed at which it is evolved depends upon the amount of surface the metal exposes, its purity, the strength of the acid solution, and the temperature. The chemical action as shown below is one of *substitution*.

It is customary to say that the metal dissolves in the acid, although the statement is incorrect. In reality, the metal and acid interact, liberating hydrogen as a gas, and forming a salt which dissolves in the water present. Zinc sulfate and zinc chlorid are both white salts that may be recovered by evaporating the excess water.

41. Physical Properties.—Hydrogen is a colorless, odorless, tasteless gas. It is the lightest gas known, being only about one-fourteenth as heavy as air, and one-sixteenth

as heavy as oxygen. One liter at standard conditions weighs almost 0.09 gram. It is *very* slightly soluble in water.

Liquids and gases have the property of intermingling through the pores of membranes (Fig. 15). This is called osmosis. Hydrogen diffuses in this manner more rapidly than any other gas, the rate of effusion of gases being inversely proportional to the square root of their densities. This makes it difficult to keep hydrogen in containers. Rubber balloons filled with hydrogen soon collapse due to

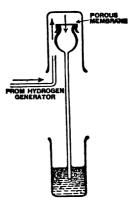


Fig. 15.—Hydrogen readily passes through membranes by osmosis.

the rapid escape of the hydrogen through the pores of the rubber.

Such metals as platinum and palladium absorb hydrogen in large quantities. The absorption of hydrogen in this manner is called *occlusion*. Considerable heat is produced as the absorption occurs, sufficient sometimes to enkindle the gas. Practical use is made of occlusion in the self-lighting gas jets and cigar-lighters.

42. Chemical Properties.—Hydrogen is not an active element. When oxygen and hydrogen are mixed no chemical action occurs. If the mixture is heated to about 800° or if a flame is brought into contact with it, the mixture explodes violently. Hydrogen and chlorin combine ex-

plosively in direct sunlight, forming hydrogen chlorid. Under suitable conditions hydrogen combines with nitrogen



Fig. 16.—Hydrogen burns but does not support combustion.

to form ammonia, a very important compound. Under certain conditions hydrogen has been made to combine with certain metals, forming hydrids. Calcium hydrid interacts with water, hydrogen being liberated.

Hydrogen burns with a very hot, pale blue, nearly invisible flame, forming water as its only product of combustion. A blazing splinter thrust into a bottle of hydrogen, as shown in Fig. 16, is extinguished, although the hydrogen catches fire and burns at the mouth of the bottle. This experiment shows that hydrogen does not support combustion.

43. Reduction.—In its narrowest sense reduction may be defined as the abstraction of oxygen from a compound. • If

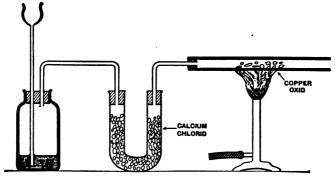


Fig. 17.—Reduction of copper oxid to metallic copper by the use of hydrogen.

we pass a stream of hydrogen over heated copper oxid, as shown in Fig. 17, the hydrogen unites with the oxygen,

forming water, and reduces the copper oxid to metallic copper. The U-tube contains granular calcium chlorid which dries the hydrogen gas before it comes into contact with the copper oxid. The equation follows:

$$\begin{array}{l}
\text{copper oxid} + \text{hydrogen} \rightarrow \text{copper} + \text{water} \\
\text{copper} \\
\text{oxygen}
\end{array}$$

It is easy to see that oxidation and reduction are opposite processes. In the above reaction the copper oxid was reduced, while the hydrogen was oxidized; the copper oxid was the oxidizing agent, hydrogen the reducing agent. Oxidation and reduction are very important processes in chemistry. Often they occur simultaneously, one substance being oxidized as another is reduced.

## 44. Uses of Hydrogen.

1. As a Reducing Agent.—We have just seen that hydrogen is a reducing agent. It is one of the most energetic,



Fig. 18.—Blimp type dirigible. (Used by U. S. Navy.)

since it unites readily with oxygen with the evolution of large quantities of heat.

2. For Its Buoyancy.—Because hydrogen is so much lighter than air, it is used for filling balloons. Its lifting power per liter is equal to the difference between the weight

of 1 liter of air (1.29 grams) and 1 liter of hydrogen (0.09 gram). There are 1000 liters in 1 cubic meter, hence for every cubic meter capacity a balloon's lifting power when filled with hydrogen is 1.2 kilograms, or 2.64 pounds. Military balloons of the Zeppelin type have a capacity of several thousand cubic meters, and can carry several tons. Fig. 18 shows an airship of the Blimp type that is used by the U. S. Navy.

3. For Its Heating Effect.—Hydrogen makes an excellent fuel. It is an important constituent of illuminating gas.

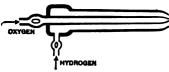


Fig. 19.—Oxy-hydrogen blow-pipe.

It is also used in the oxyhydrogen blowpipe, which consists of two concentric tubes as shown in Fig. 19. Hydrogen from a storage cylinder passes through the outer tube and is lighted

at the tip of the blowpipe. As the oxygen, passing through the inner tube, combines with the hydrogen a very hot flame is produced. Its temperature is about 2300°C. Platinum and such refractory substances as aluminum oxid are readily melted in this flame.

- 4. For Its Lighting Effect.—Although the oxy-hydrogen flame is nearly colorless, yet when it is directed against a stick of calcium oxid, or lime, a very intense white light is produced. The lime does not melt, but it is heated white hot. Any substance thus heated until it glows is said to be incandescent. The lime light was formerly much used for stereopticon work and stage illumination, but the electric arc lamp has largely taken its place.
- 5. Hydrogenation of Oils.—Hydrogen is now being used quite extensively in the hydrogenation of oils. Certain oils, such as cotton-seed oil, when treated with hydrogen in the presence of a suitable catalytic agent (finely divided nickel) are changed into solid fats that may be used as a

substitute for lard. The substance sold under the name of *Crisco* is made by this process from cotton-seed oil. Certain fish oils, when thus treated, lose their disagreeable odor and are useful for making soap.

#### SUMMARY

Hydrogen may be prepared: (1) by electrolysis; (2) by substituting a metal for the hydrogen of water; (3) by substituting a metal for the hydrogen of an acid.

Hydrogen is an odorless, tasteless, colorless gas. It is scarcely soluble in water. It is the lightest gas known. One liter weighs 0.09 gram. Hydrogen burns, but does not support combustion

Reduction is the process of abstracting oxygen from a compound.

Hydrogen is used extensively as a fuel, for reduction, for filling balloons, and in the hydrogenation of oils.

## QUESTIONS AND PROBLEMS

- 1. What precautions should be taken in preparing hydrogen by the usual laboratory method?
- 2. Would hydrogen gas make a good fuel? Is it suitable for illuminating purposes?
  - 3. How could you distinguish hydrogen from oxygen?
- 4. Should bottles of hydrogen be kept mouth upward or mouth downward? Explain.
- 5. Which metal would you use for preparing large quantities of hydrogen, zinc or iron?
- 6. Sulfuric acid is 2.04 per cent. hydrogen. How many grams of sulfuric acid are needed to prepare 10 liters of hydrogen?
- 7. How many cubic meters must a balloon hold to have a lifting power of 1000 lb. when filled with hydrogen?

### CHAPTER VI

### FUELS-ILLUMINANTS

- 45. Fuels Defined.—A fuel may be defined as any substance that readily combines with the oxygen in the air to furnish heat and light.
- 46. Characteristics of a Good Fuel.—A good fuel should have the following characteristics:
- 1. Low cost. Not only the original price of the fuel should be considered, but the cost of handling and transporting it.
  - 2. It should be easily enkindled and not burn too rapidly.
  - 3. Very little ash.
  - 4. It should have a high heat content.
  - 5. No waste products that may become a nuisance.

Let us note briefly how soft coal meets the above conditions. (1) Since it occurs in nearly every State in the Union, its original cost is not very great; it does not have to be carried very far, so the transportation charge is moderate. (2) Its kindling point is low enough to offer no difficulty in starting combustion and it does not burn up quickly. (3) The amount of ash remaining is fairly low, usually from 5 to 10 per cent. (4) It has a high heat content, as 1 gram of a good soft coal furnishes about 8000 calories when burned. The heat content of a fuel is measured in calories. One calorie is the amount of heat required to raise the temperature of 1 gram of water from 0°C. to 1°C., or through 1°C. (5) Dense clouds of black smoke and cinders pour from the chimney when soft coal is burned.

The giving off of these undesirable products as it burns forms the chief objection to the use of soft coal as a fuel.

47. Kinds of Fuel.—Under solid fuels are included peat, the various kinds of coal (cannel, bituminous, and anthracite), wood, coke, and charcoal.

A few liquid fuels are used to a large extent. The most common are petroleum, kerosene, gasoline, and alcohol.

Gaseous fuels have become quite popular. Natural gas, coal gas, water gas, producer gas, and acetylene are used quite extensively. They have a high heat content, no ash, no undesirable waste products and the cost is not excessive. Gas is especially desirable as a fuel for cooking purposes. The heat is concentrated at one point. It is so easily enkindled that it is turned off as soon as the cooking is finished and it is ready at any time for instant use. In contrast, a coal fire is enkindled with so much difficulty that when once started, it is kept burning, thus wasting the fuel.

48. Composition of Fuels.—Of the fuels named above charcoal and coke are nearly pure carbon. Hard coal is from 80 to 90 per cent. carbon. Soft coal contains slightly less carbon than hard coal. Coal always contains some uncombined or free carbon and a certain percentage of hydrocarbons. A hydrocarbon is a compound of carbon and hydrogen. Wood is composed largely of cellulose, a compound of carbon, hydrogen, and oxygen. Wood also contains considerable water.

The liquid fuels are composed almost entirely of hydrocarbons, except alcohol, which contains oxygen, carbon, and hydrogen.

The gaseous fuels consist largely of hydrogen, hydrocarbons, and carbon monoxid. Fig. 20 shows a more complete composition of several important solid fuels. The heat content of the fuels is also tabulated.

49. Products Formed by the Combustion of Fuels.—Fuels that contain carbon only, as charcoal and coke, form nothing but oxids of carbon when they are burned. Fuels that contain hydrocarbons form both carbon dioxid and water. It is of interest to note that in hydrocarbons

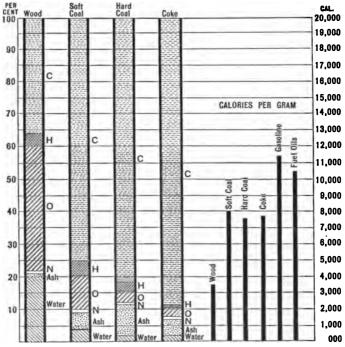


Fig. 20.—Table of fuel composition. Relative heat content of fuels.

rich in carbon, the supply of oxygen may not be great enough to oxidize both the hydrogen and the carbon. The hydrogen in such cases is oxidized and carbon set free. A part of the carbon may unite with some oxygen to form carbon monoxid. 50. Steam-heating Furnaces.—From a study of Fig. 21, we may get a good idea of the chemistry of fuels. If coal is placed upon the grate and enkindled, it is oxidized by the air that enters from beneath through the draft d. In starting a fire the damper in the pipe at b should be open

so the upward current in the chimney will increase the draft through the grate. Part of the water in the boiler is converted into steam which rises to the radiators and heats the rooms. If we close the draft d and partly close b, only a little oxygen comes into contact with the fuel and it burns slowly. It may be made to burn still more slowly, if the check draft c is open, since cold air enters and cools the fuel until it is only slightly above the kindling temperature. Throwing on fresh fuel also cools the fire. If too

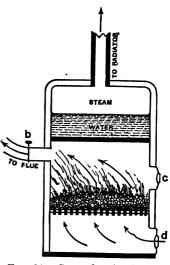


Fig. 21.—Steam heating furnace

much is added at one time, the fire may be extinguished by being cooled below the kindling temperature of the fuel.

Another chemical effect is produced when fresh coal is thrown on a fire. Carbon is a reducing agent. As the carbon dioxid which was formed by the burning of the live coals underneath comes into contact with the carbon of the fresh coal the following partial reduction occurs:

carbon + carbon dioxid → carbon monoxid.

The uncombined carbon takes part of the oxygen from the dioxid to form the monoxid. Carbon monoxid is a very poisonous gas. If the furnace door is left open, it may find its way to the living rooms above. This frequently happens when a fire is banked for the night.

51. Smoke.—Smoke contains some small particles of very finely divided ash, but its chief constituent is unburned carbon in the form of soot or cinders. Soft coal contains so much hydrocarbon that the supply of air is seldom sufficient to oxidize all the carbon. In cities where large

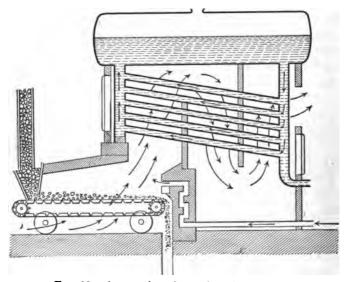


Fig. 22.—Automatic stoker and smoke consumer.

quantities of soft coal are used as fuel, the smoke nuisance is almost intolerable. It is estimated that the smoke nuisance costs the inhabitants of the city of Pittsburgh over \$10,000,000 annually. Estimates place the cost in the United States in waste of fuel, extra laundry work, and other expense at \$500,000,000 annually. This does not include discomfort and injury to health.

52. Smoke Consumers.—The unburned carbon in smoke is not only very undesirable, but it is very wasteful, since it still has a very high heat content. For these two reasons smoke consumers are being installed by large factories. The whole principle depends upon some method of increasing the supply of oxygen. Fig. 22 shows one type of smoke consumer. It has an automatic stoking device to spread the coal evenly on a chain grate. By means of baffle walls the products of combustion are forced to take a

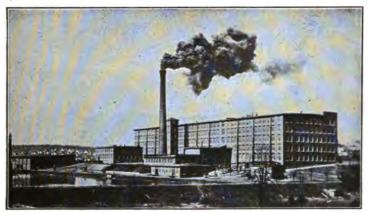


Fig. 23 —A factory that shows a dirty stack, illustrating the smoke nuisance.

circuitous path to the stack or chimney. A large air space is provided so that the combustion will be complete.

In one type of mechanical stoker the fuel is fed into a large hopper and conveyed under the fire by the sliding bottom of the feed trough that runs the full length of the stoker. As the coal rises in the trough it is distributed over the fire bars. A large volume of air is supplied to the stoker by a blower or fan. Figs. 23 and 24 show a factory before and after it was equipped with a mechanical stoker of the under-feed type.

53. Forced Draft.—The rate at which a fuel burns depends upon the rapidity with which it is supplied with oxygen. Blowing a fire makes it burn faster for two reasons: (1) the oxygen is furnished more rapidly; (2) the products of combustion are carried away by the draft. A common example of this forced draft is the use of a bellows by a blacksmith. The fire burns more rapidly and produces a more intense heat.



Fig. 24.—The factory shown in Fig. 23 after being equipped with an automatic stoker.

On ships forced draft is used when a high speed is desired. More air is forced through the fuel, causing more rapid combustion. The exhaust steam from a locomotive is forced through the smoke-stack to produce a better draft. A similar effect is produced in power plants by using very tall chimneys. Since the draft of a chimney is caused by the difference in weight between the column of gas inside the chimney and the air-column outside, it is easy to see that this difference becomes greater as the height of the chimney is increased.

54. Flame.—A flame is a burning gas. Charcoal is not

volatile and for that reason it does not burn with a flame. In the case of the candle the wax is melted and vaporized. This vapor or gas then burns with a flame. By extinguishing a candle flame, and then quickly bringing a lighted match near the wick, it may be shown that a flame is a

burning gas. It is not necessary to touch the wick to relight the candle.

55. The Bunsen Burner.—
The Bunsen burner (Fig. 25) consists of the base, the ring, and the tube or barrel. The base has a small tip or spud through which the gas enters the barrel. To secure complete combustion, air enters through the holes at the lower end of the tube and mixes with the gas before it burns at the top of the tube.

The amount of gas that enters the barrel varies with the pressure from the mains and with the size of the opening in the base. The ring is

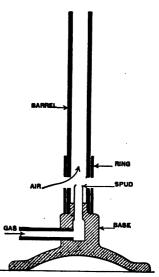


Fig. 25.—Parts of a Bunsen burner longitudinal section.

used to regulate the air supply, by opening or closing the holes in the tube. As more gas is used, more air should enter at the lower end of the tube. If the gas is partly turned off, or the pressure is too low, it will burn faster than it is supplied at the top of the tube. The relative amount of air increases until an explosive mixture is formed. It then strikes back and burns at the spud. The base then becomes hot and may melt the rubber tubing and set fire to the escaping gas. As the gas is turned partly off to lower the flame, the holes should be partly closed.

The flame of the Bunsen burner consists of two distinct cones. The outer cone is called the *oxidizing flame*, since metals held in this flame are soon oxidized. The inner cone is called the *reducing flame*. Copper oxid held in this cone is reduced to metallic copper. The tip of the inner cone is the hottest part of the flame (Fig. 26).

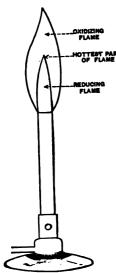


Fig. 26.—Bunsen burner, showing parts of flame.

All types of gas burners used for heating are modeled after the Bunsen burner.

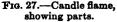
56. Luminous and Non-luminous Flames.—When the holes of the Bunsen burner are open the flame is nearly colorless and gives very little light. If we close the holes, a vellow is produced. luminous flame beaker of cold water held in this flame is soon covered with soot, showing that the combustion of the carbon is incomplete. The light which a candle, a kerosene lamp, or a gas jet gives is due to particles of unburned carbon which are heated to incandescence. This statement may be further verified by opening the holes to produce the hot, nearly colorless flame and then sprinkling particles of iron The flame becomes luminous as the

rust into the flame. The flame becomes luminous as the particles are heated white hot.

57. The Candle Flame.—The ordinary candle is made of paraffin, stearin, spermaceti, or other wax or fat. These substances contain carbon and hydrogen. When heated and enkindled, the melted wax rises by capillarity to the end of the wick where it burns with a rather complex flame. Fig. 27 shows that the flame is made up of three distinct cones. Surrounding the wick is the cone b, which consists of un-

burned gases. In the middle cone a the gases become hot enough so that a partial decomposition of the hydrocarbon occurs and some carbon is set free. By being heated to incandescence it forms the luminous cone of the candle. In the third cone c, which is narrow and almost invisible, complete combustion occurs, water and carbon dioxid being formed. In making the wicks of modern candles, one thread is drawn more tightly than the others. Thus as the candle burns the end of the wick is pulled to one side and burns in the edge of the flame. In this way it automatically trims itself.





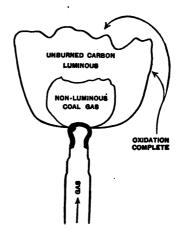


Fig. 28.—Gas jet, fish-tail burner.

58. The Gas Jet.—Fig. 28 shows the ordinary gas jet, or the fish-tail burner. To prevent the gas from burning with a smoky flame, the opening of the jet is a narrow slit. This produces a flat rather than a circular flame and better oxidation is secured. If too much surface is exposed to the oxygen the flame will be non-luminous on account of complete combustion.



Fig. 29.—Welsbach gas mantles, showing how the fibers are woven and mounted.



Fig. 30.—Welsbach gas mantles, erect and inverted types.

59. Gas Mantles.—To utilize the heating effects of gas for illuminating purposes, a mantle is suspended in the flame. Gas mantles consist of oxids of rare metals (99 per cent. thorium oxid and 1 per cent. cerium oxid). These oxids are very refractory, and when heated give a fine white light by incandescence. Such gas burners, called Welsbach burners, are equipped with devices for regulating both the amount of gas and the amount of air.

If too little air is used, carbon is deposited on the mantle. Figs. 29 and 30 show how the Welsbach mantles are made. From ramie or artificial fiber the mantle is woven, dipped into solutions of the nitrates of cerium and thorium, and then heated. The fiber burns and the nitrates are converted into oxids.

60. Acetylene as an Illuminant.—Acetylene is a hydro-carbon containing 92 per cent. of carbon and 8 per cent. of hydrogen. Since the amount

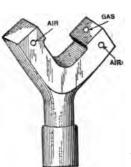


Fig. 31.—Acetylene burner.

of carbon is so large, acetylene burns with a very smoky flame, giving off large quantities of soot, unless a special burner is used. If used with a special burner to admit air, like that shown in Fig. 31, it gives a beautiful white light.

## SUMMARY

Any substance that readily combines with oxygen to furnish heat is a fuel. A good fuel should have little ash, a high heat content, should not be expensive, and should not produce undesirable products as it burns.

Fuels, whether solid, liquid, or gaseous, consist largely of carbon, hydrogen, and sometimes oxygen.

The products of complete combustion are carbon dioxid

and water. Free carbon and carbon monoxid are formed when the combustion is incomplete.

Smoke consists largely of particles of unburned carbon. Smoke consumption is based upon two principles: (1) to increase the supply of air, thus making the combustion complete; (2) to feed the coal to the fire gradually by means of an automatic stoking device.

A flame is a burning gas.

The flame of the Bunsen burner has two cones: the inner cone is the reducing flame; the outer cone, the oxidizing flame.

When combustion is complete a flame is usually nearly colorless. The luminosity of the ordinary gas flame is due to particles of unburned carbon heated to incandescence.

A gas mantle is often used to increase the efficiency of the gas flame when used for illumination.

## **QUESTIONS**

- 1. Discuss the value of wood as a fuel, using the method outlined in paragraph 46.
- 2. Discuss the value of hard coal as a fuel. Of petroleum as a fuel.
  - 3. Summarize the advantages of gas as a fuel.
- 4. Why is it dangerous to check a fire by closing the smoke damper and opening the furnace door? Why is opening the furnace door an extravagant method of checking a fire?
  - 5. Why do charcoal and hard coal burn slowly?
- 6. In the fish-tail burner the gas issues from a narrow slit. Why doesn't the gas burn with a smoky flame?
- 7. Briquettes are made by compressing coal dust mixed with some tarry material which serves as a binder. What advantage have these lumps as a fuel?
- 8. How could you determine the per cent. of ash in a sample of coal?
  - 9. Under what conditions does gasoline vapor explode?

- 10. If a kerosene lamp smokes, what are the probable causes?
- 11. Vessels at sea have used a smoke screen to escape from submarines or other hostile craft. Tell how such a screen can be produced.

Discussion Topics.—The advantages and disadvantages of steam-heating systems. Steam heat as compared with hot air and hot water.

#### CHAPTER VII

## THE GAS LAWS—STANDARD CONDITIONS

61. Measurement of Gases.—We have already learned that gases are usually measured by volume. Since the volume changes with a change of temperature or pressure, it is necessary to have some standard pressure and tem-

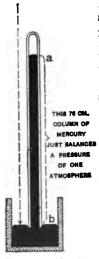


Fig. 32.—Simple barometer.

perature for use in measuring gases. The standard temperature selected is 0°C., the freezing point of water. The standard pressure is 760 mm. of mercury, or the average pressure exerted by 1 atmosphere.

G2. The Barometer.—Atmospheric pressure is measured by means of the barometer. ter. If we fill a glass tube 80 cm. long, closed at one end, with mercury and information one were it in a bowl of mercury as shown in Fig. 32, the mercury in the tube stands at a certain height above the level of the mercury in the bowl. The pressure of the air on the surface of the mercury in the bowl balances the weight of the column of mercury AB. As the air pressure is increased the mercury rises in the tube, and conversely. The vertical height of the mercury column is a measure of the

atmospheric pressure. At sea level the atmosphere sustains a column of mercury 760 mm., or 76 cm., high.

63. Effect of Pressure on a Confined Gas.—Suppose we have a bottle of 1000 c.c. capacity. If we fill this

bottle with hydrogen gas at 0°C., and put it under a pressure of 760 mm. of mercury the weight of the contained hydrogen is approximately 0.09 gram. If we increase the pressure, the volume is reduced. The weight is unchanged, however, so the density is increased. The density of any substance is the weight of 1 c.c. in grams, or of 1 cu. ft. in pounds.

Robert Boyle, in experimenting with gases, found that as the pressure increases, the volume of a gas decreases. He stated this fact in the following law which bears his name: If the temperature remains constant, the volume of a confined gas is inversely proportional to the pressure exerted upon it. If a gas has a volume of 1000 c.c. when the pressure upon it is 760 mm., its volume will be only 500 c.c., or one-half its original volume, if the pressure is doubled. Tripling the pressure reduces the volume to one-third the original volume.

Given the following PROBLEM: A 1000-c.c. bottle is filled with gas when the barometer reads 745 mm. What volume will the gas occupy at standard pressure, or 760 mm.?

Solution.—Since the pressure is to be increased from 745 mm. to 760 mm., the volume will be reduced to 745/760 of its original volume. 745/760 of 1000 c.c. equals 980.2 c.c., the volume at standard pressure.

64. Boyle's Law Shown Graphically.—The practice of plotting curves to show changes graphically furnishes a clear, concise means of representing laws in physics and chemistry. On a sheet of squared, or cross-section paper, we may use a certain horizontal line, XX', as a base from which one factor may be reckoned, and a given vertical line, YY', from which we may reckon the other factor. In Fig. 33, suppose we use the line XX' as an axis from which we measure volumes, and YY' as the vertical axis from which we measure pressures. Suppose by experiment we have obtained the following data:

Volumes		Pressures	Volumes		Pressures
(a)	2,000 c.c.	200 mm.	<b>(f)</b>	500 c.c	800 mm.
<b>(b)</b>	1,600	250	<b>(g)</b>	400	1,000
(c)	1,200	333	(h)	333	1,200
(d)	1,000	400	(i)	250	1,600
(e)	800	500	(j)	200	2,000

We may use as the origin of the curve the point of intersection, O, of the axes. Let 1 space represent 100 units. The first volume is 2000, which will be 20 spaces from the

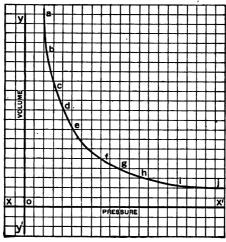


Fig. 33.—Curve of inverse proportion, representing Boyle's law graphically.

XX' axis; the corresponding pressure is 200 units, or 2 spaces from the YY' axis. This gives us the point a. Using similarly 1600 and 250, we find the point b, and so on for each pair of coördinates. Tracing a smooth line through all these points, we have a curve of inverse proportion. A little practice makes it easy to interpret laws from such curves. We see for example that as the pres-

sure is increased the point locating the curve is nearer to XX', but farther from YY', and conversely.

65. Effect of Temperature on Gas Volumes.—When gases are heated they expand. This is also true of solids and liquids. Students are familiar with the expansion of liquid mercury in thermometers. Charles, a Frenchman, found that the coefficient of expansion of all gases is the same, namely, 1/273. A gas at 0°C., the pressure remaining constant, will expand 1/273 of its volume if heated to 1°C. If heated to 100°C., its volume will be increased by 100/273, or it will then have a volume equal to 373/273 of its original volume; heated to 273°C., its volume will be doubled.

If a gas at 0°C. be cooled to -100°C. its volume will be reduced to 173/273 its original volume. Cooling to -200°C. reduces the volume to 73/273. At -273°C. the gas would theoretically have no volume. In practice all gases liquefy before that temperature is reached.

66. Absolute Temperature.—Theoretically if a gas were cooled to -273°C. and its volume reduced to zero, all molecular motion would cease, and the substance would be

C.	A.	Vol.
100	373	373
50	323	323
20	293	293
0	273	273
-100	173	173
-273	0	0

Fig. 34.—Comparison of Absolute and Centigrade scales.

absolutely without heat or at absolute zero. For this reason -273°C. equals 0°A., or zero on the absolute scale. Fig. 34 shows a comparison of the Centigrade and Absolute scales of temperature and also gives the corresponding volume changes in a gas that measures 273 c.c. at 0°C. The law of Charles may be stated as follows: If the pressure is con-

stant, the volume of a gas is directly proportional to the absolute temperature. We convert Centigrade temperatures to Absolute temperatures by adding 273° to the Centigrade reading.

Suppose we have the following problem: Given 500 c.c. of a gas when measured at 30°C. What volume will it occupy at standard temperature?

Solution.—30°C. equals 303°A.; 0°C. equals 273°A. Since the gas was cooled from 303°A. to 273°A., its volume will be reduced to 273/303 of its original volume. 273/303 of 500 c.c. equals 450 c.c., the volume of the gas at standard temperature.

67. Law of Charles Shown Graphically.—Fig. 35a shows a curve of direct proportion which represents the changes

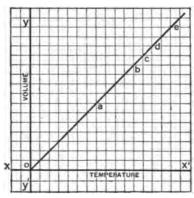


Fig. 35a.—Curve of direct proportion, representing the law of Charles

in volume a gas undergoes when heated. The absolute temperatures and volumes shown in Fig. 34 were used as coördinates in plotting this curve. The curve shows clearly that as one factor is increased the other is correspondingly increased.

Suppose we plot the curve AB, Fig. 35b, using the volumes shown in Fig. 34 as abscissas and the Centigrade tempera-

tures as ordinates. If we produce the curve backward it will intersect the YY' axis at R, a point equivalent to  $-273^{\circ}\mathrm{C}$ ., or to zero degrees Absolute. This furnishes a graphic illustration of the theoretical temperature at which all gases cease to have volume. A study of the figure also shows why Absolute temperatures rather than Centigrade must be used in solving problems involving the use of the law of Charles. If we draw dotted lines to represent volumes, the triangles

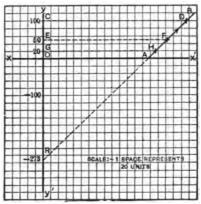


Fig. 35b.—Curve plotted to show position of absolute zero.

CRD, ERF, and GRH will all be similar. The bases CD, EF, and HG represent gas volumes at 100°C., 50°C., and 20°C. respectively. They are not proportional to CO, EO, and GO, the corresponding Centigrade temperature equivalents, but they are proportional to the respective altitudes CR, ER, and GR. These altitudes represent Absolute temperatures. Therefore the volumes of dry gases are proportional to their Absolute temperatures, but not to their Centigrade temperatures.

68. Correction of Volumes when Both Temperature and Pressure Change.—Problems involving both temperature and pressure changes are very common. In solving such

problems it is easier to combine both changes in one statement.

PROBLEM.—Given 800 c.c. of gas at 10°C. and 900 mm. pressure. What will be its volume at standard conditions of temperature and pressure?

Solution.—10°C. equals 283°A.; 0°C. equals 273°A. The temperature effect alone would reduce the volume to 273/283 of 800 c.c. The pressure is reduced, its effect alone tending to increase the volume to 900/760 of 800 c.c. The combined effect is  $273/283 \times 900/760$  of 800 c.c., or 913.8 c.c., the volume at standard temperature and pressure.

69. Difference of Levels Affects Pressure.—Students will have less trouble with the correction of gas volumes if

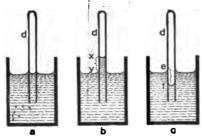


Fig. 36.—Difference of levels.

they remember that in order to have equilibrium, the pressure which a gas exerts equals the pressure upon it. In Fig. 36a, the gas d exerts a pressure of 1 atmosphere, since the liquids stand at the same level inside and outside

the tube. If we refer to Fig. 36b, we see that the pressure of the gas d plus the pressure of the column of liquid xy equals the atmospheric pressure, or barometer reading. In c of the same figure the gas d exerts a pressure equal to that shown by the barometer plus the pressure of the liquid column ef. In collecting gases by displacement of liquids, it is often impossible to so adjust the apparatus that the levels are the same. To find the correct pressure the gas exerts when the inside level is the higher of the two we must subtract from the barometer reading the length of the column xy if the liquid used is mercury. If the inside level is lower than the outside one, we must add to the barometer

reading the length of the column ef as a correction. If the liquid used is water as is usually the case, the length of the water column divided by 13.6 (since mercury is 13.6 times as heavy as water) must be subtracted from or added to the barometer reading as above.

PROBLEM.—A gas collected over mercury measures 40 c.c. when the mercury stands 90 mm. higher in the tube than outside; the temperature is 18°C., and the barometer reading 755 mm. What volume will the gas occupy at standard temperature and pressure?

Solution.—The barometer reading corrected for difference of levels equals 755 mm. less 90 mm., or 665 mm. This is the real pressure upon the gas. The corrected volume is then found as follows:  $40 \text{ c.c.} \times 273/291 \times 665/760 = 32.8 \text{ c.c.}$ 

70. Water Vapor Exerts Pressure.—As a liquid evaporates it exerts a pressure which is greatest at the point of satu-

ration. Since water evaporates faster as the temperature rises and a larger quantity is also needed to saturate a gas with water vapor, the aqueous pressure rises as the temperature is increased. In Table 3 of the Appendix, the maximum value of the pressure that water vapor exerts at different temperatures is given. Suppose we let a bottle of oxygen gas stand over water as in Fig. 37 until it is saturated with water vapor. The oxygen gas plus the water vapor exert a

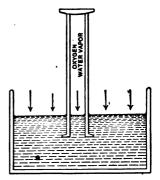


Fig. 37.—The combined pressure of the oxygen and water vapor equals the pressure of the atmosphere.

pressure equal to the atmospheric pressure as shown by the barometer. By reference to the table we can find the pressure exerted by the water vapor alone at the temperature of the gas mixture. To find the pressure of the

oxygen alone, we subtract from the barometer reading the pressure of the aqueous vapor.

PROBLEM.—Four hundred c.c. of oxygen are collected over water. The temperature is 20°C., and the barometer reads 750 mm. Find what volume the *dry* oxygen will have at standard temperature and pressure.

Solution.—From the table we find that at 20°C., water vapor exerts a pressure equal to 17.4 mm. of mercury. Then the oxygen gas alone is exerting a pressure of 750 less 17.4 mm., or 732.6 mm. This part of the operation is generally spoken of as correcting the barometer reading for pressure due to water vapor. The volume of oxygen at standard conditions may now be found by using the following equation:  $400 \text{ c.c.} \times 732.6/760 \times 273/293 = 359 \text{ c.c.}$ , the corrected volume.

Very often a correction for both aqueous pressure and difference of levels is necessary as in the following problem.

PROBLEM.—A gas collected in a tube over water measures 75 c.c. when the outside level is 67.5 mm. higher than the inner; the temperature is 20°C. and the barometer reads 757.4 mm. Find the volume of the dry gas at standard temperature and pressure.

Solution.—The barometer reading corrected for aqueous pressure equals 757.4 mm. less 17.4 mm., or 740 mm. The correction to be added for difference of levels is 67.5/13.5, or 5 mm. The true pressure of the gas is then 740 mm. plus 5 mm., or 745 mm. The volume of the gas at standard temperature and pressure equals  $75 \text{ c.c.} \times 745/760 \times 273/293$ . The result is 69.2 c.c.

#### **PROBLEMS**

- 1. Given 80 c.c. of oxygen gas at 17°C. What volume will it occupy at 40°C.?
- 2. A gas at  $-10^{\circ}$ C. measures 125 c.c. What will be its volume if the temperature is increased to 25°C.?
- 3. A gas under a pressure of 560 mm. has a volume of 645 c.c. What will be its volume under a pressure of 800 mm.?

- 4. What volume will a gas have when the pressure is 65 cm., if its volume is 950 c.c. at a pressure of 740 mm.?
- 5. Reduce to standard conditions; 95 c.c. of gas measured at 35°C. and 825 mm.
- 6. Given 100 c.c. of gas measured at 0°C. and 380 mm. pressure. What will be its volume at 273°C. and 760 mm. pressure?
- 7. Given 1 liter of gas measured at  $-20^{\circ}$ C., and 740 mm. pressure. Find its volume at 20°C. and 780 mm. pressure.
- 8. A tube contains 49 c.c. of ammonia gas collected over mercury. The inner level is 35 mm. higher than the outside level. The temperature is 18°C., and the barometer reads 747 mm. Reduce to standard conditions.
- 9. A bottle of oxygen gas is collected over water. When the temperature is 20°C., and the barometer reads 735 mm., the volume is 350 c.c. What volume will the dry gas have at standard conditions of temperature and pressure?
- 10. Given the following conditions: A gas collected over water measures 1500 c.c. at a temperature of 25°C. and a pressure of 775 mm.; the outside level is 80 mm. lower than the inside level. Find the volume of the dry gas at standard conditions.

## CHAPTER VIII

# WATER—PROPERTIES AND COMPOSITION

- 71. Abundance of Water.—Water is one of the most abundant compounds. All students of chemistry know that the water area of the earth is much greater than the land area. Nearly all common substances contain a large percentage of water. By weight about 75 per cent. of vegetables is water; milk is about 88 per cent. water; meat contains rather more than 50 per cent. water, and bread is not quite half water.
- 72. Physical Properties.—When seen in small quantities pure water is colorless; deeper layers have a blue tint. Pure water is odorless and tasteless; the taste of ordinary drinking water is due to dissolved substances, either air, carbon dioxid, or some mineral matter.

Water solidifies at 0°C., or at 32°F. As it solidifies, it expands slightly; thus ice is lighter than water and floats with about nine-tenths of its volume submerged.

Under a pressure of 760 mm. water boils at 100°C., or 212°F. The steam that is formed occupies about 1600 times the volume the water originally occupied.

Because water is so abundant and so easy to obtain in a fairly pure condition, it is used as a standard in specific heat and specific weight determinations. The use of the word specific implies a ratio. Water has its greatest density at a temperature of 4°C. At this temperature 1 c.c. of water weighs 1 gram. The ratio of the weight of unit volume of a substance to the weight of unit volume of water is its specific weight or specific density.

The specific heat of water is 1, since it requires 1 calorie of heat to raise the temperature of 1 gram of water 1°C. Since the specific heat of water is higher than that of all other ordinary substances, it heats slowly and cools slowly. Thus large bodies of water exert much influence in moderating the climate of a place.

- 73. Chemical Properties.—1. Stability.—Water is a very stable compound. Even at a temperature of 2000°C. less than 2 per cent. is decomposed. The atoms recombine as the temperature is lowered.
- 2. Action With Metals.—Water interacts readily with such metals as sodium, potassium, and calcium at the ordinary temperature, hydrogen being liberated. Zinc and magnesium decompose hot water slowly and iron interacts with steam.
- 3. Action With Oxids of Metals.—Water combines readily with certain oxids. When quick-lime, or calcium oxid is slaked, water unites with the oxid to form the compound calcium hydroxid.

As water unites with the oxids of metals, it forms a class of compounds known as hydroxids. They are known as bases. The soluble active hydroxids are called alkalis.

The oxids of non-metals, such as sulfur, carbon, and phosphorus, unite with water to form acids, as represented by the following equation:

4. Hydrates.—Water unites readily with many substances when they crystallize from water solution, forming hydrates. Several molecules of water may thus combine with one molecule of a compound.

- 5. Water Brings About Chemical Changes.—Since very few, if any, chemical reactions occur unless water is present, the water appears to act like a general catalytic agent. This action of water will be more fully discussed in a subsequent chapter.
- 6. Hydrolysis.—Hydrolysis, the decomposition of compounds by water, will also be more fully discussed in a later chapter.
- 74. Composition of Water by Volume.—We have already seen that when water is decomposed by the electric current.

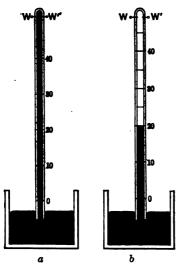


Fig. 38.—Eudiometer tube for measuring gases.

water vapor is formed. mercury rises in the tube. bined after the explosion.

2 volumes of hydrogen are liberated to 1 of oxygen. The analysis of water always yields these elements in the same proportion by volume.

It is possible to form water by the synthesis of. the elements. Fig. 38, a, shows a eudiometer tube arranged for collecting gases by mercury displacement. Suppose we introduce 20 c.c. of hydrogen and 10 c.c. of oxygen as in b of the same figure, and pass an electric spark between the platinum wires w and w'. The mixture explodes and

As the vapor condenses, the If we use 20 c.c. of hydrogen and 20 c.c. of oxygen, 10 c.c. of oxygen remain uncom-Using 30 c.c. of hydrogen and 10 c.c. of oxygen, we have 10 c.c. of hydrogen remaining uncombined. All attempts to make hydrogen and oxvgen

combine in any other ratio by volume than 2 to 1 result in failure.

75. Composition of Water by Weight.—If we collect the hydrogen and oxygen formed by decomposing a quantity of water and weigh them separately, we find eight parts by weight of oxygen to one part by weight of hydrogen. Since such a method is rather troublesome an indirect method is generally used to show the composition of water by weight. In a hard glass tube, Fig. 39, a weighed quantity of copper oxid is placed. Dry hydrogen is passed over the heated oxid, reducing the copper oxid to metallic

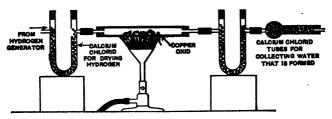


Fig. 39.—Composition of water by weight.

copper and uniting with the oxygen to form water. The water thus formed is absorbed in a previously weighed calcium chlorid tube. Suppose we start with 23.8 grams of copper oxid. After heating it weighs 19 grams. The loss of weight, 4.8 grams, is the weight of the oxygen used to form water. The calcium chlorid tube weighed 85 grams before the experiment and 90.4 grams after its completion. The gain in weight, 5.4 grams, is the weight of the water formed. 4.8 equals eight-ninths of 5.4 grams. Therefore eight-ninths, or 88.88 per cent. of water is oxygen; one-ninth, or 11.11 per cent. is hydrogen.

76. Water of Crystallization.—We have already learned that water combines with certain substances when they crystallize. Such crystals appear to be dry, even when

powdered. Water of crystallization should not be confused with water mechanically held by a crystal either adhering to it or enclosed by it. That water of crystallization is chemically combined with the substance is shown by the fact that it follows the law of definite proportions.

When such crystals are heated they lose water, the color usually disappears as well as the luster, and a powder is formed. Such removal of water of crystallization is called dehydration and the substance is then said to be anhydrous. For example, crystallized copper sulfate has a blue color and a vitreous luster. When heated it loses water and crumbles to a dull gray powder. If water be again added to this gray anhydrous copper sulfate, a blue solution is formed. From this solution hydrated copper sulfate crystals can be recovered by evaporating the excess water

Sodium carbonate crystallizes with 10 molecules of water, nearly 62 per cent. by weight; sodium sulfate has 10 molecules of water of crystallization, or 55.9 per cent.; copper sulfate crystallizes with 5 molecules of water, over 36 per cent. Some crystals, as sodium chlorid and potassium chlorid, have no water of crystallization.

- 77. Efflorescence.—A crystal that loses its water of crystallization when exposed to the air at ordinary temperature is said to be efflorescent. If we put on a scale pan a few crystals of sodium sulfate or sodium carbonate, and put enough shot in the other pan to counterpoise them, the crystals show a loss of weight in a short time. Water is given off and the crystals lose their luster, crumbling to a powder. Efflorescence occurs more readily in a very dry atmosphere than during damp rainy weather.
  - 78. Deliquescence.—Crystals of zinc chlorid, magnesium chlorid, and calcium chlorid take moisture from the air on exposure, and become wet, or even dissolve in the water thus absorbed. This property is known as deliquescence. It is much more pronounced in damp weather.

Crystals like common table salt that attract moisture so that a slight film forms on their surface are called hygroscopic. Common table salt usually contains as an impurity a slight trace of some deliquescent substance. becomes wet in damp weather and "packs."

Deliquescent substances are used extensively for drying

other substances. In the experiments on reduction and on determining the composition of water, the hydrogen was dried by passing it through a tube filled with calcium chlorid, a delisubstance. The quescent water formed in the latter experiment was absorbed by the same compound. 40 shows a desiccator used for drying compounds in the laboratory. The lower compartment is filled with deli- Fig. 40.—Desiccator. quescent crystals



oxygen

79. Hydrogen Peroxid.—Although 2 hydrogen atoms unite directly with only 1 atom of oxygen, yet the compound hydrogen peroxid, having the formula H<sub>2</sub>O<sub>2</sub>, may be formed indirectly. By treating sodium peroxid or barium peroxid with a cold dilute acid the following reaction occurs:

Barium peroxid + sulfuric acid →

| barium hydrogen oxygen (2 atoms) sulfur hydrogen peroxid + barium sulfate hydrogen oxygen (2 stoms)

Pure hydrogen peroxid is a heavy syrupy liquid. very unstable, but a dilute aqueous solution keeps fairly well if the light is shut off. Commercial hydrogen peroxid is a 3 per cent. solution of hydrogen peroxid in water. Its decomposition products are water and oxygen.

An element just as it is being liberated from a compound is said to be in the *nascent state*. It is then more active than at any other time. In the decomposition of hydrogen peroxid, the oxygen is very active as it is being set free. For this reason hydrogen peroxid is a very good oxidizing agent.

Oxidizing agents destroy the color of many organic substances; they also kill bacteria. Thus hydrogen peroxid is used as an antiseptic and a disinfectant. It is also used extensively as a bleaching agent, especially for animal fibers, wool, silk, hair, and feathers, which might be injured by certain cheaper bleaching agents.

80. Law of Multiple Proportions.—Frequently the same elements unite to form a series of compounds; thus hydrogen and oxygen form water  $(H_2O)$  and hydrogen peroxid  $(H_2O_2)$ . The law of definite proportions is true for each of these compounds, water being composed of 11.11 per cent. of hydrogen and 88.88 per cent. of oxygen, and hydrogen peroxid having 5.8 per cent. hydrogen and 94.1 per cent. oxygen. In water there are 8 parts by weight of oxygen to 1 of hydrogen; in hydrogen peroxid there are 16 parts by weight of oxygen to 1 of hydrogen.

After studying several series of compounds, John Dalton formulated the following law of multiple proportions: When two elements unite to form a series of compounds, if we consider a fixed weight of one element, which we may call "A," then the weights of the other element, "B," will be in the ratio of small whole numbers. In the above example the weight of the hydrogen or element "A" being 1, then the weights of oxygen or element "B" are 8 and 16 or the ratio of 1 to 2, small whole numbers. 16 is a multiple of 8, hence the name multiple proportions.

### SUMMARY

Water is one of the most abundant compounds. Water is colorless, odorless, and tasteless. It freezes at 0°C. and boils at 100°C. One cubic centimeter of water at 4°C. weighs 1 gram.

Chemically water interacts with several metals. It unites with the oxids of metals to form bases. It unites with the oxids of non-metals to form acids. It unites with many compounds as they crystallize forming hydrates.

The loss of water of crystallization when crystals are exposed to the air is called efflorescence.

Some substances absorb water from the air and dissolve in the water thus absorbed. This property is known as deliquescence.

Hydrogen peroxid is used as an oxidizing agent; as a disinfectant; and as a bleaching agent.

When two elements unite to form a series of compounds, if we consider a fixed weight of one element, "A," then the weights of the other element, "B," will be in the ratio of small whole numbers.

# QUESTIONS AND PROBLEMS

- 1. How would natural conditions be affected if water contracted upon solidifying?
- 2. Explain how water moderates climatic extremes of temperature.
  - 3. Why is water so important from a chemical standpoint?
- 4. Suppose we mix 45 c.c. of hydrogen and 15 c.c. of oxygen and explode the mixture. What gas remains and what is its volume?
- 5. If we repeat the experiment given in problem 4, using 35 c.c. of oxygen and 50 c.c. of hydrogen, which gas will remain and what volume will it occupy?
- 6. Would you prefer to buy crystals of washing soda (sodium carbonate) that had been kept in stoppered bottles or in open boxes, if the price per pound were the same? Explain.
- 7. Why should bottles of calcium chlorid be kept tightly stoppered? Bottles of calcium oxid, or quick-lime?
  - 8. What advantage is gained by putting small unstoppered

# 74 WATER—PROPERTIES AND COMPOSITION

bottles of calcium chlorid in the cases of clocks, electrical machines, and accurate balances?

- 9. Why is hydrogen peroxid usually sold in brown-colored bottles?
  - 0. How would you determine the per cent. of water in milk?
- 11. How could you use anhydrous copper sulfate as a test for water?

### CHAPTER IX

## SOLUTION—CRYSTALLIZATION

81. Solution.—One of the very important properties of water is its ability to dissolve certain substances. The substance that goes into solution, or dissolves, is called the solute. The liquid that is used to bring about solution is the solvent. If we dissolve a small crystal of potassium permanganate in a liter or more of water, every drop will have a purple tint, thus showing that in solution the particles are finely divided. If we taste a drop of a solution of common salt taken from the surface, it is found to be as salty as a drop from any other part of the solution. In solutions the solute does not settle upon standing, or separate from the solvent.

A solution has the following characteristics: (1) It is homogeneous, having the same nature throughout; (2) the particles of the solute are very finely divided and can not be removed by filtration; (3) the solute does not separate from the solvent upon standing as does material in suspension. A solution may be defined as a homogeneous mixture consisting of a solvent and the solute.

The question whether solution is a physical or a chemical change is one upon which chemists are still in doubt. It seems reasonably certain that chemical action occurs in dissolving some compounds. In other cases the action appears to be physical. When water is the solvent, the solute often unites with it to form hydrates. In such a case this part of the action is doubtless chemical, but if the hydrate then dissolves in the excess water that is present, the action is probably physical.

82. Solution of Solids, Liquids, and Gases.—The solute may be a solid, a liquid, or a gas. Water is one of the best solvents known, as many different substances are more or less soluble in water. Other well-known solvents include alcohol, gasoline, turpentine, ether, and carbon tetrachlorid. An alcoholic solution of a non-volatile substance is called a *tincture*. For example, tincture of iodin is a 5 per cent. solution of iodin in alcohol.

When two liquids are mutually soluble, they are said to be miscible. Alcohol and water are miscible in all proportions. Oil and water are immiscible. When an oily liquid is vigorously shaken with water the finely divided particles of oil remain temporarily suspended in the water forming an emulsion. Milk is a good example of an emulsion as the fat globules remain suspended for some time before the cream separates. Several substances may be used to make emulsions more permanent. Gums have this property. The cleansing action of soap is largely due to its ability to form emulsions with grease. In making mayonnaise dressing egg yolks are added to make the emulsion of olive oil permanent.

Most gases are to some extent soluble in water; in some cases several volumes dissolve in one volume of water.

83. Saturation.—If we add a few crystals of common table salt to 100 c.c. of water they dissolve readily, forming a dilute solution. As more salt is added, the solution becomes more concentrated. When the solvent holds all the salt it can at a given temperature, the solution is said to be saturated with salt at that temperature.

When we speak of a dilute solution we refer to a solution containing a relatively small proportion of the solute; a concentrated solution contains a relatively large proportion of the solute.

The ratio between the weight of the solute and the weight of

the solvent required to make a saturated solution is known as the solubility of the solute at that temperature.

84. Effect of Temperature on Solubility.—The solubility of a solid depends upon the nature of the solid itself, upon the solvent used, and also upon the temperature. In general an increase in temperature increases the solubility of a solid. For example, 100 grams of water at 30°C. dissolve only 44 grams of potassium nitrate, while at 70°C. the same weight of water dissolves 140 grams of potassium nitrate.

As in the case of solids, the solubility of liquids increases as the temperature rises, until the boiling point of one of the liquids is reached.

Gases, however, are less soluble at higher temperatures. Heating a solution of a gas causes some of the gas to escape. The bubbles that arise when water is first heated are air bubbles. Their evolution is due to a decrease of solubility with increased temperature.

The solubility curves of Fig. 41 show clearly the effect of temperature and the nature of the solid on solubility.

- 85. Effect of Pressure on the Solubility of Gases.—When a gas is forced into a solvent under increased pressure its solubility is much increased. In fact the solubility of a gas is directly proportional to the pressure at which the gas is supplied. This statement is known as Henry's law. It is put to practical use in bottling carbonated waters and in charging soda fountains, where carbon dioxid is forced into the solvent under a pressure of from 5 to 10 atmospheres. When soda water is drawn from the fountain the carbon dioxid gas escapes with effervescence.
- 86. Speed of Solution.—We may hasten the speed at which a solid dissolves in three ways: (1) by stirring. Agitating the mixture brings fresh portions of the solvent in contact with the solute; (2) by powdering the solid. Since solution occurs only at the surface of a solid, powdering the solute increases the amount of surface that comes in

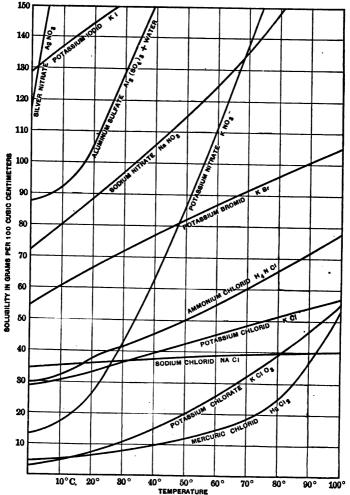


Fig. 41.—Curves showing the effect of temperature on solubility.

contact with the solvent; (3) by heating, since an increase in temperature increases the solubility.

87. Freezing Point and Boiling Point of Solutions.— A solution always freezes at a temperature lower than the freezing point of the pure solvent. When an unsaturated solution begins to freeze, the pure solvent solidifies and the solute it contained forms with the rest of the solvent a more concentrated solution. Thus the freezing point is lowered still more until the solution finally becomes saturated. A saturated solution has a constant freezing point. For example, a saturated solution of sodium chlorid freezes at -22°C.

The boiling point of a solution also differs from that of the pure solvent. As the solution of a non-volatile solid boils the solvent disappears by evaporation and the solution becomes more concentrated until it is finally saturated. In the meantime the boiling point gradually rises as the solution becomes more concentrated.

If the solute is more volatile than the solvent, the solution generally boils at a *lower* temperature than the pure solvent, and at the same time it becomes more dilute.

88. Crystallization.—If we cool a hot saturated solution, the excess solute is thrown out of solution in the form of crystals. The shape of the crystal depends upon the nature of the substance. Salt crystals are cubes; alum crystals are octahedra. The shape of the crystal is peculiar to the substance and identification from the form of the crystal is often possible (Fig. 42). Crystals are generally formed when a liquid freezes or solidifies. They are also thrown out of a saturated solution, or precipitated, when it is evaporated.

Crystallization is much used in purifying chemicals. Suppose we have two salts dissolved in water. Since practically no two substances have the same solubility, the *less* soluble salt will crystallize first when the solution is cooled

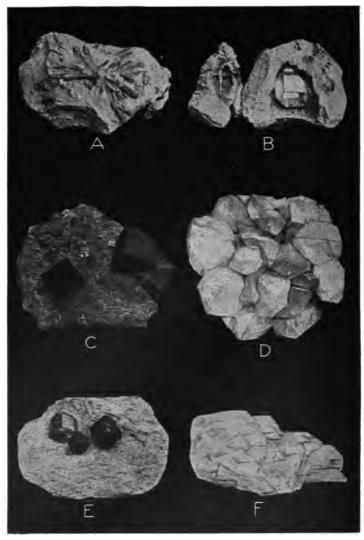


Fig. 42.—Plate of crystals. a. Rubellite. b. Quartz crystal in matrix. c. Galena. d. Quartz crystals. e. Garnets on rock. f. Gypsum.

or evaporated. The other salt remains in the "mother liquor." By further evaporation other crystals are obtained. The first crop of crystals is the purest. The process is known as fractional crystallization. The crystals may be still further purified by dissolving them in pure water and recrustallizing.

If the solution is stirred while crystallization is taking place, finer crystals are formed. Small crystals thus rapidly produced are generally purer than large crystals formed more slowly, since the latter are more apt to have incorporated in them some of the mother liquor. If crystals that contain water thus mechanically held are heated they decrepitate. Steam is formed within the crystal and its expansion causes the crystal to burst open with a snapping sound.

- 89. Supersaturated Solutions.—If we saturate a solution with ordinary "hypo" at a temperature of 60° or 70°C., and then cool it slowly to a lower temperature without disturbance, the excess solute is not deposited as crystals. Such a solution is said to be supersaturated. When a fragment of "hypo" is added to such a solution, crystals begin to form immediately. The crystallization continues until all the excess solute has separated, leaving a solution saturated at the lower temperature. Stirring a supersaturated solution or scraping the inside of the containing vessel usually starts the crystallization. Some substances readily form supersaturated solutions; others show this tendency to a very slight degree only.
- 90. Colloidal Suspensions.—Such substances as glue, gums, resins, starch, and gelatine do not crystallize. They are known as colloids. With liquids they form colloidal suspensions. Colloids in suspension differ from other substances in suspension as follows: (1) They can not be removed by filtration, as the particles are fine enough to pass through the filter; (2) they are as uniformly distributed as particles in solution; (3) they do not settle upon standing.

Colloids in suspension differ from crystalloids in solution in three ways: (1) While such a suspension is more or less transparent, yet a beam of light is diffused as it passes through the suspension; (2) The particles are larger than those of a solute. This is shown by dialysis. If we enclose both crystalloids and colloids in a vegetable or animal membrane and suspend them in pure water, the crystalloids readily pass through the membrane while the colloids are retained. Colloids were first separated from crystalloids in this manner by Graham in 1861; (3) unlike crystalloids, colloids do not markedly affect either the freezing point or the boiling point of the suspension.

91. Importance of Colloids.—Since the work of Graham more attention has been given to the study of colloids and their importance in many industries is being recognized. The fertility of soils depends to some extent upon their colloidal nature. The finely divided particles have an extensive surface for adsorption, or the condensation of water and fertilizing materials upon the surface. Many colloids are spontaneously deposited from suspensions as "gelatinous" masses. Considerable water is usually included in such semi-solid masses and they can not as a rule be redissolved. One illustration of their use is in the preparation of the sensitive film for photographic "dry" plates. In paint, varnish, rubber, paper, and glass manufactures colloids play an important part. The varying ability of asphalt pavement to resist the wear of traffic is said to be due to the fineness of the particles in the colloidal semisolid mass.

### SUMMARY

A solution is a homogeneous mixture consisting of a solvent and the solute.

Liquids that are mutually soluble in each other are said to be miscible.

The concentration of a solution is the weight of solute in a given quantity of solvent. In a dilute solution the concentration is small; in a concentrated solution it is large; in a saturated solution the concentration is at its maximum.

An increase of temperature increases the solubility of solids; it decreases the solubility of gases. An increased pressure increases the solubility of gases in liquids.

The speed of solution may be hastened: (1) by stirring; (2) by raising the temperature; (3) by powdering the substance.

Cooling a saturated solution causes a part of the solute to separate as crystals. Evaporation produces the same effect.

## **OUESTIONS**

- 1. How would you proceed to prepare a saturated solution of a salt?
- 2. Given a solution of sodium sulfate. How could you tell whether it is unsaturated, saturated, or supersaturated?
- 3. If you were given a solution containing sodium chlorid and potassium nitrate, how would you separate the two salts? Would the method be suitable for use at a temperature of 25° to 30°C.? Refer to the curves of solubility and explain.
- 4. When emulsions are used as medicines, why should the bottle be thoroughly shaken before using?
  - 5. Why do soda fountains sometimes burst or explode?
- 6. Account for the rapid effervescence when a glass of "soda water" is drawn. Why do bubbles of gas continue to rise more slowly as the liquid stands for a time?
- 7. Why are crystals of sugar often found in preserves that have stood a long time?
- 8. If you had a mixture of a sugar solution and gelatine, how could the two be separated?
- 9. Why do vegetables cook faster in a strong salt solution than in fresh water?
  - 10. How does a solution differ from a chemical compound?

### CHAPTER X

# PURIFICATION OF WATER—HARDNESS

92. Impurities in Water.—Since water is such a good solvent, and no substance is absolutely insoluble, it is practically impossible to obtain pure water. The impurities present in water may be held: (1) in suspension; (2) in solution. Because of its buoyant effect water holds material in suspension. When water is in motion, upward currents are more or less prevalent, thus making it possible for water to hold more material in suspension. The amount of material water can carry depends upon the size and density of the particles; it also increases as the velocity of the water is increased.

Rain water has very little matter in solution. It is soft water. Ground water contains considerable mineral matter in solution, since water is such a good general solvent. Water that contains more than 50 parts of mineral matter dissolved in 1,000,000 parts of water is classed as hard water. Very hard water has over 100 parts per million. Some especially hard waters have 400 parts of mineral matter per 1,000,000.

93. Kinds of Impurities.—Impurities in water are classed as: (1) organic; (2) inorganic, or mineral. Organic matter consists of bacteria, sewage, and other forms of animal and vegetable matter in various stages of decomposition or decay. As plants and animals decay, ammonia is formed. This ammonia is slowly oxidized first to nitrites and then to nitrates. The presence of more than a trace of ammonia, nitrites, or nitrates in drinking water indicates sewage con-

tamination, or that the water is unwholesome. Much organic matter in water renders it unfit for drinking purposes, since such matter, though often harmless in itself, forms a breeding ground for all kinds of bacteria.

Either harmless or disease-producing bacteria may be present in drinking water. Epidemics of typhoid fever, dysentery, and cholera have often been traced to contaminated water supply. Typhoid fever has been nearly stamped out in cities where proper methods of purifying the water supply have been installed.

The nature of mineral matter in solution in water depends upon the composition of the soil and rock through which the water flows. Compounds of calcium, magnesium, sulfur, and iron are among the most common substances found in hard water. Since calcium compounds are found in the bones and teeth, their presence in water that is to be used for drinking purposes is desirable.

94. Methods of Purification.—Matter in suspension may be removed from water: (1) by sedimentation; (2) by sedimentation with coagulum; (3) by filtration.

Organic matter is to a greater or less degree destroyed by (1) aëration; (2) light; (3) ultra-violet rays; (4) boiling; (5) cold; (6) use of chemicals.

Non-volatile matter in solution is removed by distillation.

- 95. Sedimentation.—Water that is turbid or roily is clarified by letting it stand in shallow tanks or reservoirs. The particles that are heavier than water soon fall to the bottom on account of the influence of gravity, since there are no upward currents in the undisturbed water. This method of purification is usually preliminary to filtration.
- 96. Sedimentation with Coagulum.—Aluminum hydroxid is an insoluble compound, very gelatinous in its nature. When aluminum sulfate is added to water, certain mineral matter that is often present unites with it to form the hydroxid. As this bulky gelatinous precipitate settles,

nearly all material in suspension, including a large per cent. of the bacteria, is carried down with it. When the water does not contain the mineral matter needed to precipitate the aluminum hydroxid, lime-water is added with the aluminum sulfate to produce the *coagulum*. The hardness of the water is slightly increased by this method of purification.

97. Filtration.—Water from wells and springs is purified by natural soil filtration. As the water trickles through the



Fig. 43a.—Filtration beds showing connection with water mains.

soil the impurities in suspension are strained out. Destruction of the bacteria and organic matter occurs by oxidation. The efficiency of this method of purification depends upon the nature of the soil and the distance the water travels through uncontaminated soil. A sandy or gravelly soil is best. If the well is in a valley and near-by houses and stables are situated on higher ground, the soil through which the water flows may become contaminated with pathogenic bacteria. Filtration through such a soil is a menace.

Slow Sand Filters.—City water is often filtered through layers of sand and gravel acres in extent and several feet thick. Layers of charcoal may be used between the sand and gravel to remove coloring matter and gases having disagreeable odors. At the bottom the filtered water collects in tile drains which transmit it to the city mains. A gelatinous layer soon collects on the top thus aiding the purification, partially because of more perfect filtration



Fig. 43b.—A portion of the same filtration beds filled with sand ready for filtration.

and partially because microörganisms that destroy bacteria collect in this layer. As the rate of filtration becomes more and more retarded, it is necessary to scrape off this surface layer occasionally. These filtration plants are expensive to install, since they should be covered to prevent freezing (see Fig. 43a). In the presence of sunlight certain plants known as algæ grow readily in water reservoirs. They are sometimes called "pond-scum." Some varieties secrete

an oily substance that gives to the water a disagreeable, fishy odor (see Fig. 43b).

Mechanical Filters.—Mechanical filters are rapid sand filters that are generally used with coagulation systems. The water is run into large tanks and treated with the chemicals as in the coagulum method described above. The partially clarified water is then strained rapidly through the sand and gravel layers in the mechanical filter. Fig. 44 shows a mechanical filter of the gravity type.



Fig. 44.—Gravity type of mechanical filter.

In Fig. 45 a pressure filter is shown. When mechanical filters need to be cleaned water is forced through them in the reverse direction, the impurities being carried into the sewer with the wash water. The revolving rakes shown in Fig. 45 aid the cleansing process by breaking up the bed of filtering material.

98. Aëration.—Only surface water comes into contact with the oxygen of the air. When the water is agitated fresh portions are brought to the surface. In some reservoirs fountains have been installed which cause the water

to spout up into the air and flow back over a large surface in thin layers. In some cases compressed air bubbles up through the water in the reservoir. In still other cases aëration is accomplished by letting the water flow over a series of cascades as it enters the reservoir. Aëration oxidizes organic matter and some of the bacteria are de-

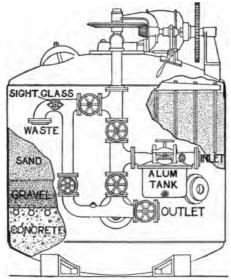


Fig. 45.—Mechanical filter of the pressure type.

stroyed. Gases having disagreeable odors are also removed by this method of purification (Fig. 46).

99. Light.—Sunlight readily destroys bacteria. It is not very practical, however, since only the surface layers are affected; it also fosters the growth of algæ, or pond-scum, which may impart an undesirable odor or taste to the water.

100. Ultra-violet Rays.—Rays from the sun are of three kinds: (1) heat rays; (2) light rays; (3) ultra-violet rays. The last named can not be detected by any of the senses

but they do affect a photographic plate and they are very active in producing numerous other chemical effects. They readily destroy bacteria. They can be prepared artificially, as by the Cooper-Hewitt mercury vapor lamp. Using such a lamp in a quartz tube, Victor Henri showed that water flowing fairly rapidly through an apparatus, in which it was exposed to the ultra-violet rays, was rendered practically free from bacteria.



Fig. 46.—Purification of water by aëration.

101. Boiling.—Very few bacteria can withstand a temperature of 100°C. for more than a few minutes. Hence boiling water for from 5 to 15 minutes destroys most germs it may contain. On a large scale this method is impracticable. When used on a small scale, the water should be subsequently aërated to destroy its "flat" taste.

- 102. Cold.—Many bacteria are destroyed at the freezing temperature of water. Ice is purer than the water from which it is obtained, probably containing less than 5 per cent. as many bacteria. It is never safe, however, to use ice from polluted water, since some bacteria can withstand freezing, or even the extremely low temperature of liquid air.
- 103. Use of Chemicals.—1. The use of ozone in water purification has already been discussed. Its use is gaining in favor, since it forms oxygen and an excess in water is not undesirable.
- 2. Chlorin is sometimes used to destroy bacteria in water. It is usually liberated from sodium hypochlorite or from "chlorid of lime." Sometimes it is introduced by letting it flow from cylinders of liquid chlorin. In the nascent state it is a very active germicide. Any excess in the water is very undesirable.

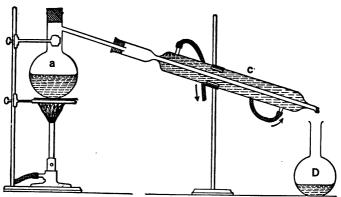


Fig. 47.—Apparatus illustrating distillation.

3. Copper sulfate is used to destroy algae in city reservoirs. If waters are known to be polluted, it is sometimes used as a germicide. So small an amount as 1 part in 10,000,000 parts of water is said to destroy disease germs.

Because of its poisonous nature, there is considerable popular prejudice against its use.

104. Distillation.—Distillation is a complex process consisting of evaporation and subsequent condensation. Since mineral matter in water often interferes with its use for chemical purposes, distilled water is used extensively in

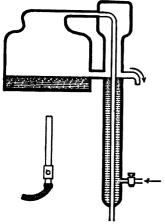


Fig. 48.—Continuous action still.

chemical operations. The water to be distilled is put in the distilling flask a, as shown in Fig. 47, and heated to boiling. The condenser c consists of two concentric tubes through the outer of which cold water flows continuously. The water vapor condenses in the inner tube and is collected in a receiver at d.

Water may be obtained in a reasonably pure state by distillation. Since any gases or volatile matter will readily

be driven off by the heat, the first portion of the distillate should be rejected. The non-volatile matter remains in the distilling flask. Fig. 48 shows one type of continuous action still. The water that is used for condensation later flows into the still. Thus it is somewhat warmed by the heat of condensation.

The student should not get the idea that distillation is used only for the purification of water. It is extensively used in purifying other liquids. In fact practically any liquid that does not decompose at the temperature of its boiling point may be purified in this manner.

Liquids that have different boiling points may usually be separated by fractional distillation. To illustrate,

petroleum is composed of several substances boiling at different temperatures. The petroleum is heated at a low temperature until the oils having a very low boiling point, such as naphtha, petroleum ether, gasoline, and benzine, are all volatilized and condensed. The temperature is raised until gas oil distillates are vaporized. At a still higher temperature various grades of lubricating oil and paraffin oil are obtained.

105. Hard Waters.—The most common mineral matter in hard waters consists of calcium, magnesium, and iron compounds. When soap is added to a water containing a calcium compound, it unites chemically with the calcium to form a gritty insoluble compound known as "lime soap." Chemically it is calcium stearate. Hard water is said to "curdle" soap. Magnesium forms a similar compound with soap. Suds can not be formed with hard water until all the calcium and magnesium compounds have been precipitated.

Waters that contain bi-carbonates of calcium, magnesium, and iron are known as temperary hard waters. When water containing carbon dioxid in solution comes into contact with limestone (calcium carbonate) the bi-carbonate of calcium is formed as follows:

Calcium bi-carbonate is much more soluble than the calcium carbonate. When water containing the bi-carbonate is boiled the reaction is reversed:

$$\begin{array}{ccc} \text{calcium} & \text{bi-carbonate} & \rightarrow & \uparrow \\ & \text{calcium} & \text{carbonate} + \text{water} + \text{carbon dioxid.} \end{array}$$

The less soluble calcium carbonate is precipitated. Thus waters containing bi-carbonates that behave chemically in a similar manner are called temporary hard waters because they may be softened by boiling.

Permanent hard waters usually contain sulfates of calcium and magnesium. These substances are not precipitated when the water is boiled.

106. Objections to the Use of Hard Waters.—1. Laundry Purposes.—If suds can not be produced until all the mineral matter in hard water is precipitated, evidently considerable

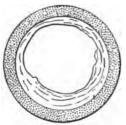


Fig. 49.—Boiler scale.

soap will be wasted if hard water is used for laundry purposes. The gritty precipitate is objectionable too, since it accumulates on the sides of tubs and in the pores of the fabric, giving the garment a dingy appearance after washing.

2. Steam Boilers.—Large quantities of water are evaporated to produce steam for power purposes. If hard

water is used, its mineral matter remains after evaporation forming an incrustation known as "boiler scale" (see Fig. 49). This incrustation is a very poor conductor of heat and more fuel is needed to produce steam when even a thin scale is present. Engineers estimate that an incrustation of a magnesium compound  $\frac{3}{64}$  in. thick requires 25 per cent. more fuel.

Hard waters also produce corrosion or pitting in steam boilers, thus decreasing the life of the boiler or its flues. Dissolved oxygen and carbon dioxid are probably active in such corrosion.

3. Other Industries.—Mineral matter is especially objectionable in water used in the dyeing industry. The color may be altered, or uneven dyeing or spotting may result, if hard water is used. Hard water may cause stains

upon the leather in leather manufactures, or upon paper in the paper industry. In soap factories, sugar refineries, and chemical works hard water is objectionable.

107. Softening Hard Waters.—Several compounds are used as water softeners. The most common are lime, sodium carbonate, sodium fluorid, and sodium aluminate. Graphites are quite widely used to facilitate the removal of boiler scale. Because they are inexpensive, sodium carbonate (washing soda) and lime are the most widely used chemical softeners. Borax is very useful for softening hard water for household use, but it is too expensive to be used on a large scale.

Permutit is the name given to a compound recently manufactured to soften hard waters. It is a sodium aluminum silicate that exchanges its sodium for the calcium and magnesium of hard waters. It can be regenerated by letting it stand for a few hours in contact with a strong solution of sodium chlorid.

## SUMMARY

Impurities in water are: (1) organic, or (2) inorganic. They may be held in suspension or in solution.

Impurities in suspension may be removed as follows: (1) sedimentation; (2) sedimentation with coagulum; (3) filtration.

Organic matter may be destroyed in several ways: (1) aëration; (2) light; (3) ultra-violet rays; (4) boiling; (5) cold; (6) use of chemicals.

Matter in solution in water may usually be removed by distillation. Liquids having different boiling points may be separated by fractional distillation.

Hard water contains mineral matter in solution. Very hard waters may contain several hundred parts per million. If the mineral matter is removed by boiling the water is classed as temporary hard water. Permanent hard water can not be softened by boiling,

Hard waters waste soap, corrode boilers and produce boiler scale, and interfere in the manufacture of many different products.

Hard waters may be softened by using sodium carbonate, lime, borax, and permutit.

#### **OUESTIONS**

- 1. Distinguish between "pure water" and "wholesome water."
- 2. If you were making up solutions in the laboratory would you use filtered water or distilled water? Give reasons for your answer.
- 3. Why is a good microscope needed in a sanitary water analysis?
- 4. How would you test to determine the presence of mineral matter in solution in water?
- 5. Try to find out why water must be kept at the boiling temperature for some minutes to kill bacteria.

Topics for Reference.—Purification of your city water supply. Use of the Pasteur filters.

## CHAPTER XI

# CONSTITUENTS OF THE AIR—NITROGEN

- 108. Weight and Pressure.—We frequently use the expression "as light as air." While air is very light when compared with water and some other substances, yet 1 liter of air at standard temperature and pressure weighs 1.293 grams. One cubic yard of air weighs about 2 pounds. The air in a good-sized schoolroom weighs several hundred pounds. Since air has weight it exerts pressure. A column of air whose base is 1 square inch and whose length is the height to which the atmosphere extends weighs 14.7 pounds. Hence the pressure of the air on each square inch of surface is 14.7 pounds. This is known as the pressure of 1 atmosphere. A column of mercury 76 centimeters high exerts an equal pressure.
- 109. Constituents of the Air.—The most important constituents of the air are oxygen, nitrogen, carbon dioxid, and water vapor. The average per cent. of each constituent by volume is as follows:

Pe	Per cent.	
Oxygen	21	
Nitrogen		
Carbon dioxid		
Water vapor, variable, almost never more than	2	

Less important constituents of the air occupy about 1 per cent. of the total volume.

110. Air a Mixture.—There are several evidences that air is a mixture and not a compound.

- 1. Its composition varies slightly in different localities and in the same locality at different times.
- 2. Air dissolved in water has a higher proportion of oxygen than atmospheric air. A compound in solution follows the law of definite proportions.
- 3. A compound has a definite boiling point. Evidently air is a mixture since the nitrogen in liquid air vaporizes first leaving nearly pure liquid oxygen.
- 4. When oxygen and nitrogen are mixed in the same proportion as in air, there is no evidence of any chemical action, such as the evolution of light or heat; neither is there evidence of any chemical action when the constituents are separated.
- 111. Preparation of Nitrogen.—1. By removing the oxygen from the air it is possible to obtain nitrogen mixed with the remaining constituents. If we ignite a piece of phosphorus in a small crucible floating on water and cover it with an inverted bottle of air, the phosphorus combines with the oxygen to form phosphorus pentoxid. As the pentoxid dissolves the water rises in the bottle taking the place of the oxygen which was removed. The bulk of the remaining gas is nitrogen.
- 2. Pure nitrogen may be obtained by heating ammonium nitrite and collecting the gas by water displacement. In practice a solution containing ammonium chlorid and sodium nitrite is heated since the ammonium nitrite decomposes too rapidly. The reaction is as follows: ammonium chlorid + sodium nitrite ->

 nitrogen
 sodium

 hydrogen
 nitrogen

 chlorin
 oxygen

112. Properties.—1. Physical.—Nitrogen is a colorless, odorless, tasteless gas. It is slightly lighter than air;

1 liter at standard temperature and pressure weighs 1.26 grams. It is slightly soluble in water. Nitrogen is non-poisonous, but animals die in the pure gas from oxygen starvation.

- 2. Chemical.—Nitrogen is an inert gas. It neither burns nor supports combustion. Indirectly it may be made to combine with hydrogen forming ammonia. When an electric spark is passed through a mixture of oxygen and nitrogen, nitric oxid, a compound of nitrogen and oxygen is formed. Nitrogen unites with some metals at high temperatures to form nitrids. The nitrids of magnesium and aluminum are the most common. While compounds of nitrogen are usually formed with considerable difficulty, they are unstable and quite easily decomposed. Nitroglycerin and nitro-cellulose (smokeless powder) are examples of nitrogen compounds that readily decompose with great violence.
- 113. Uses of Nitrogen.—Nitrogen in the air is a diluent. It makes combustion less rapid in air than in pure oxygen. It also gives bulk to the air, increasing its buoyant force and its pressure.

Plants need nitrogen to make proteins, or albumin. They can not use free nitrogen from the air, however, but must obtain it from the nitrogen compounds in the soil. The nitrogen cycle in nature is a most important one. From the soil plants secure nitrogen compounds, water, and mineral matter, and with the carbon dioxid obtained from the air, they make proteins, or plant albumin. As decay occurs ammonia, nitrites, and nitrates are formed and restored to the soil to be used for subsequent nutrition of plants.

Very often this natural cycle is interfered with, the plants being used for animal food and transported long distances; thus the nitrogen is removed from the soil and not returned by decay. The soil becomes impoverished and new crops can not be grown unless some artificial fertilizer is used to take the place of the above natural fertilizing process. There are several sources of nitrogen compounds that are available:

1. All plant and animal refuse, as from slaughter houses, fish canneries, garbage, and sewage, is rich in nitrogen compounds.

Both garbage and sewage are often wasted, and in many cities large sums of money are paid for the disposal of this waste. In some cities they are emptied into rivers, or into the ocean. Garbage is sometimes incinerated. The larger cities now have reduction plants for handling garbage. These plants recover grease by treatment with steam or a petroleum solvent, and the nitrogen-bearing residues are dried and sold to fertilizer manufacturers under the name of tankage. Some attention has been given to methods of treating sewage to destroy dangerous bacteria so that the valuable waste nitrogen compounds may be used as fertilizers.

- 2. Nitrate beds have been found in South America, principally in Chile, which furnish stores of nitrogen fertilizers.
- 3. Certain bacteria grow in nodules on the roots of clover, peas, and beans (see Fig. 50). They have the ability to take nitrogen and oxygen from the air and convert them into compounds that plants can use. Thus clover, the cow pea, and the Soy bean, while excellent forage crops, at the same time restore nitrogen compounds to worn-out soils. These bacteria are cultivated at Experiment Stations and can be secured by farmers.
- 4. Several chemical processes have been devised for the fixation of atmospheric nitrogen.
- (a) Large electric plants have been constructed, especially in Norway, for passing a huge electric discharge through moist air. Nitric oxid is formed which unites with more oxygen and water to form nitric acid. The nitric acid acts on slaked lime forming calcium nitrate

which is an excellent fertilizer. As the action is reversible the oxids of nitrogen must be immediately removed to prevent decomposition. This is known as the Birkeland-Eyde process.

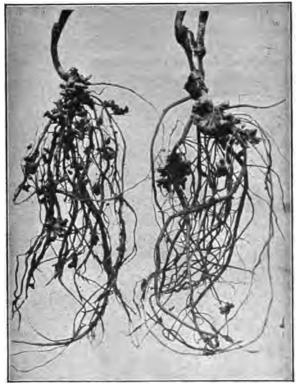


Fig. 50.—Nodules containing bacteria that take nitrogen from the air.
(J. Russell Smith, Commerce and Industry, by permission.)

(b) Nitrogen and hydrogen also combine when an electric spark is passed through the mixture; a catalytic agent may be used. Ammonia is formed; it is one of the best fertilizers. This action is also reversible.

- (c) A nitrid of aluminum forms ammonia when treated with water.
- (d) Nitrogen passed over heated calcium carbid forms calcium cyanamid, an excellent fertilizer, since it forms ammonia when treated with superheated steam, or by its interaction with soil water.
- 114. Carbon Dioxid.—If a bottle of lime-water is left exposed to the air a crust of calcium carbonate soon forms on its surface. This shows the presence of carbon dioxid in the air, since lime-water is a test for carbon dioxid. The amount of carbon dioxid varies only slightly. Several factors tend to increase the amount in the air: (1) animals inhale oxygen and exhale carbon dioxid; (2) the carbon of fuels unites with the oxygen of the air to form carbon dioxid; (3) during decay carbon dioxid is one of the decomposition products of both animal and vegetable matter.

The amount of carbon dioxid in the air is decreased by the following factors: (1) Plants use carbon dioxid to make starch. The carbon of the dioxid unites with water taken in through the roots forming starch and liberating oxygen. (2) As the solid rock of the earth's crust disintegrates, or weathers, carbon dioxid in water solution unites with certain substances forming carbonates.

The carbon dioxid and oxygen cycle in nature may be summarized as follows: Animals inhale oxygen and exhale carbon dioxid; plants absorb carbon dioxid during photosynthesis and give out oxygen.

Animals and plants are thus mutually dependent, since by the action of both, the supply of oxygen and carbon dioxid in the air is kept nearly constant.

115. Water Vapor in the Air.—Deliquescent substances become wet when exposed to the air. A glass of ice water standing in a warm room soon becomes covered with drops of water. These tests, as well as the fact that rain falls occasionally, show that the air contains water vapor.

The amount of water vapor the air can hold is its capacity. It is usually expressed in grains per cubic foot. The capacity increases as the temperature rises. The amount of water vapor the air does hold at a given time is called its absolute humidity. Absolute humidity is also expressed in grains per cubic foot. It depends upon several factors, but chiefly upon proximity to a large body of water from which evaporation may occur. The relative humidity equals absolute humidity.

Raising the temperature decreases the

relative humidity and the air feels drier since the capacity is increased by a rise in temperature. Lowering the temperature lowers the capacity and *increases* the relative humidity, making the air feel damp. When the relative humidity becomes 100 per cent., the *dew-point* is reached. A further cooling of the air then results in precipitation of some of the moisture as rain, snow, etc.

A high relative humidity makes the heat oppressive in summer and the cold seem more severe in winter. We say the air is "heavy." In reality 1 liter of water vapor at standard temperature and pressure would weigh only 0.81 gram. When the relative humidity is too low, the perspiration evaporates rapidly and the skin feels dry; when the relative humidity is very high, the perspiration does not evaporate and the skin is clammy and sticky. We are most comfortable when the relative humidity is from 40 to 50 per cent.

116. Ventilation.—Since we exhale carbon dioxid and inhale oxygen the air in a closed room will soon show a higher percentage of carbon dioxid than 4 parts in 10,000. Unless some method of exchanging this exhaled air for pure air is used, it soon becomes foul not only because there is a decided increase in the per cent. of carbon dioxid present, but organic impurities given off from the lungs make it still more impure. The relative humidity is increased

at the same time, thereby increasing the discomfort. Ventilation consists in exchanging the foul air of a room or building for pure air drawn from out of doors. The principle of ventilation depends upon the fact that warm air is lighter than cold air. In window ventilation an opening near the top of the room furnishes an exit for the impure air as colder, pure air enters through an opening nearer the floor. In many large buildings pure air is forced into the room by motor-driven fans. The New Jersey State law requires that 1800 cu. ft. of fresh air be supplied per hour for each pupil in a schoolroom.

117. Minor Constituents of the Air.—Dust particles are always present in the air. The spores of yeasts, molds, and bacteria float in the air and thus have ready access to uncovered food. Traces of a large number of gases are present in the air.

Argon is an inert gas that is present in the air to the extent of about 1 per cent. It forms no compounds and so far as known has no use whatever. The fact that it escaped discovery until little more than two decades ago and the method by which it was isolated give it an historic interest.

Neon (new), krypton (hidden), and xenon (stranger) are three other elements that have been discovered in the air within the last 20 years. Like argon they are inert, having no known compounds.

Helium (sun) as its name implies was first discovered in the sun's atmosphere. It was recently discovered in our atmosphere. It is present in very minute quantities. It is a light, inert gas. No compounds of helium are known.

118. Liquid Air.—If we open the valve of an inflated tire and hold the hand in the escaping air, we notice a marked cooling effect. Cooling always occurs when gases expand. As they are compressed, heat is produced. The liquefaction of gases depends upon these facts. In making liquid air, a pressure of from 3000 to 4000 lbs. per square

inch is used; then the air escapes through a needle valve. The escaping air in the liquefier circulates around the compressed air in an inner pipe thus cooling it to a very low temperature. As this cooled air then escapes and expands some of it liquefies (see Fig. 51).

Liquid air is nearly colorless. Under ordinary atmospheric pressure it boils at about -190°C. Of course it is a

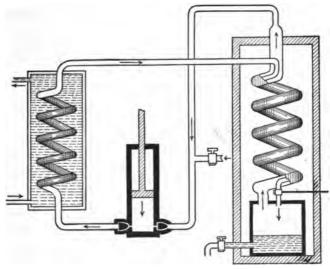
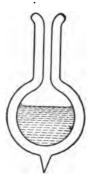


Fig 51.—Linde's apparatus for liquefying air.

mixture of liquid nitrogen and liquid oxygen. Since nitrogen boils at a lower temperature than oxygen, it evaporates first; the temperature then rises gradually. Finally nearly pure oxygen, a blue liquid boiling at  $-183^{\circ}$ C. is left. Mercury, alcohol, and carbon dioxid all solidify in liquid air. Tin becomes very brittle; lead becomes elastic. Rubber immersed in liquid air is made so brittle that it can readily be broken into fragments. Some idea of its very low temperature is obtained if we remember that the

difference between its temperature and that of ice is nearly twice as great as the difference between ice and boiling water.

Liquid air is used to produce very low temperatures. It is used as a source of oxygen commercially. Nitrogen from liquid air is sometimes used in the making of calcium cyanamid for fertilizers.



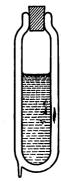


Fig. 52.—Dewar flask, cross-section.

Fig. 53.—Thermos bottle.

Dewar devised a flask for keeping liquid air. Fig. 52 shows that it is a double-walled container; the space between the two walls is a vacuum. Since a vacuum is a non-conductor of heat and since the glass is silvered to prevent the transmission of radiant heat, liquid air keeps fairly well inside such a flask, as it boils quite slowly. The thermos bottle is constructed on the same principle (Fig. 53).

#### SUMMARY

Air has weight and exerts pressure. Its chief constituents are oxygen, nitrogen, carbon dioxid, and water vapor.

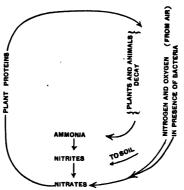
Nitrogen may be obtained from the air by removing the oxygen with some chemical, such as phosphorus. Pure nitrogen is prepared by heating a mixture of ammonium chlorid and sodium nitrite.

Nitrogen is odorless, colorless, tasteless; it is non-poison-

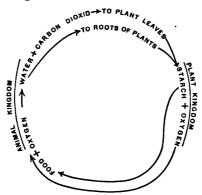
ous. Nitrogen is slightly soluble in water and a little lighter than air.

Nitrogen neither burns nor supports combustion; it is quite inert. Under certain conditions it unites with oxygen, hydrogen, and a few metals.

Nitrogen compounds are needed by plants to form proteins. The nitrogen cycle in nature is a very important one. The accompanying sketch summarizes the natural changes.



The oxygen-carbon dioxid cycle is also very important as the following diagram shows:



The ratio of the amount of water vapor the air does hold to what it could hold if saturated is its relative humidity. It is always expressed in per cent.

Argon, neon, xenon, krypton, and helium are all inert gases found in the air. No use is known for any of them.

Gases may be liquefied by compressing them and then letting them expand. All gases have been liquefied, helium at a temperature within 2° of absolute zero.

# QUESTIONS AND PROBLEMS

- 1. What changes would result if the per cent. of oxygen in the air were increased?
- 2. Find the weight of the air in a room 30 ft. long, 20 ft. wide, and 14 ft. high.
- 3. Discuss the importance of nitrification, or the fixation of atmospheric nitrogen.
- 4. Why are traces of nitrogen compounds found in the air after a thunder storm?
- 5. How could you obtain air free from carbon dioxid? Free from water vapor?
- 6. If a ton of hard coal in burning removes about 2 tons of oxygen from the air and forms about 3 tons of carbon dioxid, why do the constituents in the air vary so little in their relative amounts?
- 7. Liquid air becomes blue when it stands for some time. Explain.
- 8. Why does liquid air boil vigorously when poured into a vessel standing on a cake of ice?
- 9. Would it be a good idea to stopper a thermos bottle or a Dewar flask containing liquid air? Explain.
- 10. Can it ever rain while the air is being warmed? Would expansion or compression of the air be more likely to produce rain?

Topics for Reference.—Liquefaction of gases; Onnes. The isolation of the rare elements in the atmosphere.

### CHAPTER XII.

# ATOMIC THEORY—ATOMIC WEIGHTS

119. Equivalent Weights.—In the analysis of water we found that 1 part by weight of hydrogen combines with 8 parts by weight of oxygen to form the compound. Here 1 part by weight of hydrogen is equivalent to 8 parts by weight of oxygen. If we analyze hydrogen chlorid, HCl, we learn that 1 part of hydrogen combines with 35.5 parts by weight of chlorin. Similar analyses show that:

1 part by weight of hydrogen combines with 4.66 parts by weight of nitrogen to form ammonia; with 16 parts by weight of sulfur to form hydrogen sulfid.

Such metals as magnesium do not readily combine with hydrogen but they replace hydrogen from acids by substitution. Experiment shows that approximately 12 grams of magnesium are needed to replace 1 gram of hydrogen. Experiment shows that 23 grams of sodium replace 1 gram of hydrogen. In all cases the lowest weight in any combination is that of hydrogen. For that reason hydrogen is used as the standard in determining equivalent weights. We may define the equivalent weight of any element as the number of grams of that element that will combine with or replace 1 gram of hydrogen. In all weight relations in chemistry if the weight of one substance is taken in grams the weight of the others is reckoned in grams; if one quantity is weighed in pounds, the other is also taken in pounds. Tabulating the above results we see that:

8 grams of oxygen combine with	1 gram of hydrogen
35.5 grams of chlorin combine with	1 gram of hydrogen
4.66 grams of nitrogen combine with	1 gram of hydrogen
16 grams of sulfur combine with	1 gram of hydrogen
12 grams of magnesium replace	1 gram of hydrogen
23 grams of sodium replace	1 gram of hydrogen

120. Combining Weights.—Further study shows that the above elements combine with each other in the ratio of their equivalent weights. Therefore they are often called combining weights.

1 gram of hydrogen combines with	8 grams of oxygen
4.66 grams of nitrogen combine with	8 grams of oxygen
12 grams of magnesium combine with	8 grams of oxygen
23 grams of sodium combine with	8 grams of oxygen
12 grams of magnesium combine with	35.5 grams of chlorin
23 grams of sodium combine with	35.5 grams of chlorin
12 grams of magnesium combine with	16 grams of sulfur
23 grams of sodium combine with	16 grams of sulfur

The student can readily see how important it is to the manufacturer of chemical compounds to use the exact combining weights. For example, our grandmothers used for baking powder 2 parts of cream of tartar to 1 of baking soda. When these compounds interact 188 parts by weight of cream of tartar unite with 84 parts by weight of baking soda. The ratio is 2.23 to 1. A large baking powder factory using the correct instead of the approximate proportions saves about 12 per cent.

Some elements have more than one combining weight. In water, the ratio of hydrogen to oxygen is 1 to 8; in hydrogen peroxid, the ratio of hydrogen to oxygen is 1 to 16. The higher combining weight is always a multiple of the lower.

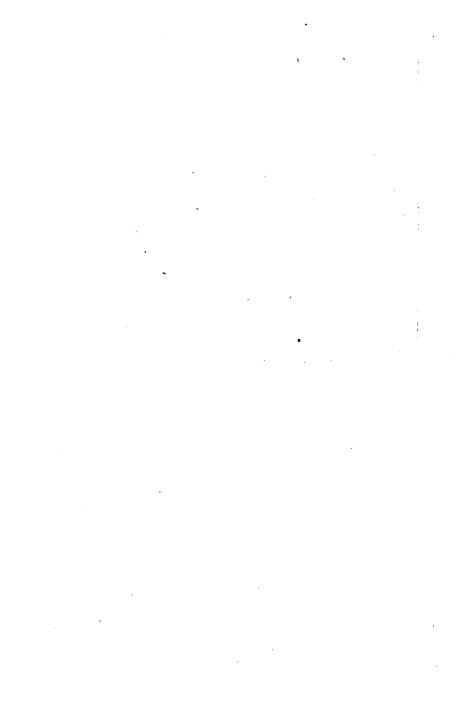
121. The Atomic Theory.—John Dalton proposed the atomic theory as an explanation of the nature of matter. The atomic theory assumes:



John Dalton (1766–1844) was an English chemist and philosopher. He is best known in chemistry for his development of the atomic theory. He studied the absorption of gases by water and determined the composition of carbon dioxid. In the development of his atomic theory, Dalton stated the laws of definite proportion and multiple proportion.

Toseph Louis Gay-Lussac (1778-1850) was a distinguished French chemist. He was the first to announce that oxygen and hydrogen unite to form water in the simple ratio of one volume of oxygen to two volumes of hydrogen. Further investigations led to his discovery of the law of volumes for He isocombining gases. lated boron and devised new methods of analyzing organic compounds.





- 1. That matter is made up of very small particles called atoms; these atoms are indivisible by chemical means.
  - 2. That the atom of an element has a definite weight.
  - 3. That atoms of different elements have different weights.
  - 4. That chemical affinity is the attraction between atoms.

Since atoms do not divide when chemical changes occur, and their weight is definite, it is easy to understand why the law of definite proportion by weight must be true. Adding an atom to a compound or removing it from a compound changes the weight of that compound by a definite amount. In the compound water 2 atoms of hydrogen combine with 1 of oxygen; in the compound hydrogen peroxid, 2 atoms of hydrogen combine with 2 of oxygen. This explains the law of multiple proportions. The 2 atoms of hydrogen in each compound have the same weight; in hydrogen peroxid the 2 oxygen atoms weigh twice as much as the oxygen present in a molecule of water. When two elements unite to form a series of compounds, each atom added increases the weight by a definite amount and the ratios of all the weights may be expressed by small whole numbers.

122. Atomic Weights.—Since atoms are so small, they can not be weighed directly. By indirect methods their relative weights have been determined. The lightest atom known is the hydrogen atom. Its weight is taken as 1. Since the oxygen atom is 16 times as heavy, the atomic weight of oxygen is 16. The atomic weight of any element is the ratio of the weight of its atom to the weight of the hydrogen atom.

The atomic weights used in these chapters are approximate atomic weights. In reality the oxygen atom is only 15.88 times the weight of the hydrogen atom; or if we take oxygen as 16, hydrogen is 1.008. It is more scientific to use the weight of the hydrogen atom as the standard for determining atomic weights. It is much more convenient

in making computations to use oxygen as the standard, using the weight 16. The table showing the atomic weights of the elements is given on the back cover. Students are not expected to memorize atomic weights; they are to be used for solving problems.

123. Chemical Formulas.—We are now able to understand a fuller significance of chemical formulas. The formula,  $H_2O$ , represents: a. 1 molecule of water; b. it shows that each molecule of water contains 2 atoms of hydrogen and 1 atom of oxygen; c. it represents 2 parts by weight of hydrogen (each atom of hydrogen having a weight of 1) and 16 parts by weight of oxygen; d. it stands for 18 parts by weight of water.

In any chemical formula the small number that follows any symbol shows the number of such atoms in the molecule. For example,  $C_{12}H_{22}O_{11}$ , the formula for cane sugar, shows that each molecule of sugar contains 12 atoms of carbon, 22 atoms of hydrogen, and 11 atoms of oxygen.

A number that precedes a formula shows the number of molecules used. For example,  $5H_2SO_4$ , stands for 5 molecules of sulfuric acid, each molecule containing 2 hydrogen atoms, 1 sulfur atom, and 4 oxygen atoms. The formula for copper nitrate,  $Cu(NO_3)_2$ , shows that each molecule contains 1 atom of copper, 2 atoms of nitrogen, and 6 atoms of oxygen. The formula is written  $Cu(NO_3)_2$  instead of  $CuN_2O_6$ , because the group of elements  $(NO_3)$  behaves like a single element.

124. Percentage Composition.—If we know the formula of a compound and have a table of atomic weights, it is a matter of simple arithmetic to find the per cent. of each element in that compound. First, the molecular weight is equal to the sum of the weights of all the atoms in the compound. Suppose we desire to find the percentage composition of the compound potassium chlorate, formula KClO<sub>3</sub>. From the table of atomic weights we find the following:

K, 1 atomweight equals 39.0	
Cl, 1 atomweight equals 35.5	
$O_3$ , 3 atomsweight equals $48.0$ (3 $\times$ 16)	
molecular weight, 122.5	
39, the weight of potassium ÷ 122.5, total weight, =	
31.83 per cent. potassium.	
35.5, the weight of chlorin ÷ 122.5, total weight, =	
28.98 per cent. chlorin.	
48, the weight of oxygen ÷ 122.5, total weight, =	
39.18 per cent. oxygen.	

Often the compound contains water of crystallization. Sodium carbonate may be taken as an example of such a compound. Its formula is  $Na_2CO_3 \cdot 10H_2O$ . The formula shows that 10 molecules of water have crystallized with 1 molecule of sodium carbonate to form the hydrate. The period indicates water of crystallization; it is not a sign of multiplication here.

```
2 \times 23, or 46 parts by weight are sodium, Na 1 \times 12, or 12 parts by weight are carbon, C 3 \times 16, or 48 parts by weight are oxygen, O 10H_2O = 10 \times 18, or 180 parts by weight are water, H_2O 286 parts by weight are crystallized sodium carbonate.
```

 $46 \div 286 = 16.08$  per cent. of sodium.

 $12 \div 286 = 4.20$  per cent. of carbon.

 $48 \div 286 = 16.78$  per cent. of oxygen.

 $180 \div 286 = 62.93$  per cent. of water, eight-ninths of which is oxygen; one-ninth, hydrogen.

125. Simplest Formula of a Compound.—By analysis in the laboratory we may determine the percentage composition of a compound. By using the atomic weights, it is then possible to find the relative number of particles or atoms in the molecule of the compound. This gives the simplest formula.

Suppose we have the following data: A compound is found by analysis to be 75 per cent. carbon and 25 per cent. hydrogen. Now the carbon atom is 12 times as heavy as the hydrogen atom. Since we can have no fractions of atoms, if we divide 75 per cent. by 12, and 25 per cent. by 1, the quotients will give the relative number of carbon and hydrogen atoms in each molecule of the compound.

$$75 \div 12 = 6.25$$
  
 $25 \div 1 = 25.00$ 

For every 6.25 carbon particles there are 25 hydrogen particles. The simplest ratio of these two numbers is 1 to 4. Therefore, the simplest formula having the percentage given above is CH<sub>4</sub>, 1 carbon atom to 4 hydrogen atoms.

A certain compound contains carbon, 40 per cent.; hydrogen, 6.66 per cent.; and oxygen, 53.33 per cent. Find its simplest formula.

$$40 \div 12 = 3.33$$
  
 $53.33 \div 16 = 3.33$   
 $6.66 \div 1 = 6.66$ 

3.33, 3.33, and 6.66 have the ratios 1, 1, and 2. Therefore, the simplest formula of the compound is CH<sub>2</sub>O. We may summarize as follows: To find the simplest formula of a compound, divide the per cent. of each element by its atomic weight. Find the ratios of the quotients in small whole numbers. Write the symbols of each element, using enough atoms to correspond to the ratio found.

### SUMMARY

The equivalent weight of an element may be defined as the number of grams of that element that will combine with or replace 1 gram of hydrogen.

Equivalent weights are sometimes called combining

weights or reacting weights. Some elements have more than one reacting weight.

The atomic theory assumes:

- 1. That matter is made up of atoms.
- 2. These atoms are indivisible.
- 3. The atom of each element has a definite weight.
- 4. Atoms of different elements have different weights.
- 5. Chemical affinity is the attraction between atoms.

The atomic weight of any element is the number that tells how many times its atom is as heavy as the hydrogen atom.

Chemical formulas show the composition of a compound; how many atoms of each element are present in 1 molecule; and, by the use of the atomic weights, the parts by weight of each element in the compound.

### **QUESTIONS AND PROBLEMS**

- 1. State fully the meaning of the following formulas: HNO<sub>3</sub>; KCl; CuSO<sub>4</sub>; Ca(OH)<sub>2</sub>; 4ZnCl<sub>2</sub>; CuSO<sub>4</sub>·5H<sub>2</sub>O; Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>; FeSO<sub>4</sub>·7H<sub>2</sub>O.
- 2. What is the difference between CuSO<sub>4</sub> and CuSO<sub>4</sub> · 5H<sub>2</sub>O? How much weight would you expect 10 grams of the latter to lose if heated to 100°C.?
- 3. Find the percentage composition of the following: Fe<sub>2</sub>O<sub>3</sub>; HgO; CO<sub>2</sub>; C<sub>2</sub>H<sub>5</sub>OH; NaCl; Ca(NO<sub>3</sub>)<sub>2</sub>; Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.
- 4. What per cent. of aluminum sulfate is water, its formula being Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 18H<sub>2</sub>O?
- 5. A compound contains carbon and hydrogen. Carbon equals 92.31 per cent.; hydrogen equals 7.69 per cent. Find its simplest formula.
- 6. Find the simplest formula of a compound of the following composition: calcium, 40 per cent.; carbon, 12 per cent.; oxygen, 48 per cent.
- 7. Find the simplest formula of a compound of the following composition: sodium, 28.05 per cent.; carbon, 29.26 per cent.; hydrogen, 3.66 per cent.; oxygen, 39.02 per cent.

- 8. Find the simplest formula of a compound of the following composition: carbon, 40 per cent.; hydrogen, 6.66 per cent.; oxygen, 53.33 per cent.
- 9. Find the simplest formula of a compound of the following composition: phosphorus, 56.36 per cent.; oxygen, 43.64 per cent.
- 10. Crystallized sodium sulfate has the formula, Na<sub>2</sub>SO<sub>4</sub>-10H<sub>2</sub>O. Which is cheaper, crystallized sodium sulfate at 10 cents per pound, or anhydrous sodium sulfate at 16 cents per pound?
- 11. Find the simplest formula of a compound having the following composition: carbon, 64.86 per cent.; hydrogen, 13.52 per cent.; oxygen, 21.62 per cent.

### CHAPTER XIII

## GAS LAWS-MOLECULAR WEIGHTS

126. Gay-Lussac's Law.—We found by experiment that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam. Further experiments show the following results concerning combining volumes of gases:

1 volume of hydrogen + 1 volume of chlorin  $\rightarrow$  2 volumes of hydrogen chlorid.

1 volume of nitrogen + 3 volumes of hydrogen  $\rightarrow$  2 volumes of ammonia.

The facts regarding relative combining volumes of gases were first summarized by Gay-Lussac in the law that bears his name: The combining volumes of gases and the volume of the product, if it is a gas, may be expressed by small whole numbers. This law applies only to gases. For example, (?) volumes of carbon +4 volumes of hydrogen  $\rightarrow 2$  volumes of marsh gas. Carbon is not gaseous, therefore Gay-Lussac's law does not apply to it, and we do not know its combining volume in relation to hydrogen and to the product.

127. Avogadro's Theory.—We have now studied three gas laws, namely: the law of Boyle, the law of Charles, and the law of Gay-Lussac. From a consideration of these laws and also from a study of the relations between reacting weights and volume weights, Avogadro proposed the following theory: Under the same conditions of temperature and pressure, equal volumes of all gases have the same number of molecules. To illustrate, 1 liter of hydrogen has the

same number of molecules as 1 liter of oxygen or any other gas at the same temperature and pressure. The actual number of molecules present is of little importance, but the theory that the number is the same for all gases is very important in chemistry.

128. Molecules of Gaseous Elements Contain Two Atoms.—From a consideration of Avogadro's theory, it is possible to show that the molecule of an ordinary gaseous element contains 2 atoms. By experiment we have, 1 volume of hydrogen +1 volume of chlorin  $\rightarrow$  2 volumes of hydrogen chlorid. Since by Avogadro's theory the number of molecules in equal volumes is the same we may write from the above, 1 molecule of hydrogen +1 molecule of chlorin  $\rightarrow$  2 molecules of hydrogen chlorid.

But, hydrogen chlorid has the formula HCl, hence each molecule has 1 atom of hydrogen. Since 1 molecule of hydrogen furnishes the hydrogen for 2 molecules of hydrogen chlorid, the hydrogen molecule must split into 2 atoms. Similar reasoning shows that the chlorin molecule also contains 2 atoms.

From the equation for the formation of steam we may show that the oxygen molecule contains 2 atoms.

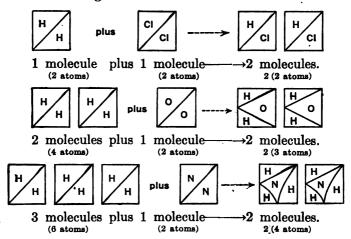
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2 vols. hydrogen +1 vol. oxygen \rightarrow 2 vols. steam. 2 mols. hydrogen +1 mol. oxygen \rightarrow 2 mols. steam.
```

Since 1 molecule of oxygen furnishes the oxygen for 2 molecules of steam, each containing 1 oxygen atom, therefore the oxygen molecule must split into 2 atoms. In these proofs we assume that 1 volume contains 1 molecule. For the actual number in 1 liter, see paragraph 4.

The application of Gay-Lussac's law and Avogadro's theory may be represented graphically. In the following diagrams each square represents one volume of gas, and the equation is based upon experiment. By Avogadro's theory, the ratio is not changed if we substitute the word molecule

MOLE. 121

for the word volume, assuming that each volume contains 1 molecule. The symbols represent atoms. The weight remains unchanged.



In a similar manner we may show that the molecules of all ordinary gaseous elements contain 2 atoms. The molecules of some elements that are liquid or solid at the ordinary temperature do not contain 2 atoms when vaporized. For example, mercury and iodin have at high temperatures only 1 atom to the molecule; phosphorus has 4; sulfur, 2, 4, or 8, varying with the temperature.

- 129. Mole Defined.—A mole may be defined as the gram-molecular weight of a substance. One mole of any substance is its molecular weight times 1 gram. For example, 1 molecule of hydrogen, having 2 atoms, has a molecular weight of 2. One mole of hydrogen is 2 grams. One mole of oxygen is 32 grams; of hydrogen chlorid, is 36.5 grams; 1 mole of water is 18 grams.
- 130. Mole of Any Gas Occupies 22.4 Liters.—Suppose we desire to find out what volume 1 mole of hydrogen at standard temperature and pressure occupies. One mole of

hydrogen is 2 grams, or, using the more accurate figure, 2.016 grams. One liter of hydrogen at standard temperature and pressure weighs 0.09 gram. Then 1 mole occupies  $2.016 \div 0.09$ , or 22.4 liters. From Avogadro's hypothesis, a mole of one gas should occupy the same space as 1 mole of any other gas. One mole of oxygen occupies 22.4 liters, since  $32 \div 1.429 = 22.4$ . Testing a large number of gases, we find that the facts agree with the theory and that 1 mole of any

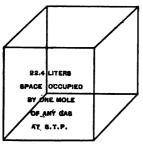


Fig. 54.—22.4 liter box.

gas occupies 22.4 liters space at standard conditions of temperature and pressure (Fig. 54).

Weight of a Compound.—Since 1 mole of a gas at standard conditions occupies 22.4 liters, we have an easy method of finding the molecular weight of compounds that vaporize without decomposition. Suppose we construct a

box that holds just 22.4 liters (see Fig. 54). If we weigh such a box, fill it with the vapor of the substance at standard conditions, and then weigh it again, the difference in weight in grams is numerically equal to the molecular weight of the substance.

EXAMPLE.—A 22.4-liter box weighs 2000 grams; when filled with ammonia gas at standard conditions the weight is 2017 grams. Therefore, 22.4 liters of ammonia weigh 17 grams, and the molecular weight of ammonia is 17.

It is not always practicable to collect the gas and weigh it at standard temperature and pressure. Any temperature and pressure may be used and the weight corrected by the use of the law of Boyle and the law of Charles.

132. To Find the Molecular Weight of Non-volatile Compounds.—A molar solution contains 1 mole of solute per 1000 grams of solvent. Pure water freezes at 0°C. If we

dissolve 1 mole of alcohol, 46 grams, in 1000 grams of water the solution freezes at -1.89°C. One mole of sugar dissolved in 1 liter of water also lowers the freezing point 1.89°. The lowering of the freezing point is proportional to the number of molecules present in a given weight of solvent. Therefore, we may find the molecular weight of a substance by finding how many grams must be dissolved in 1000 grams of water to lower its freezing point 1.89°C. This is known as the freezing point method of finding molecular weights. It does not apply to acids, bases, and salts.

The molar solution of a non-volatile substance raises the boiling point 0.52°C. For example, if we dissolve 1 grammolecule, or mole, of sugar in 1000 grams of water, the solution boils at 100.52°C. We may find the molecular weight of a substance by determining the number of grams that must be dissolved in 1000 grams of water to raise its boiling point 0.52°C. The boiling-point method of determining molecular weights does not apply to acids, bases, and salts. The reason will be given in a later chapter. Raoult was the first to observe the relationship between the mole and the freezing point and boiling point of solutions. The above statements are known as Raoult's laws.

133. Correct Formulas.—In the last chapter we learned how to find the *simplest* formula of a compound when its composition is known. By determining its molecular weight, it is possible to find its *correct* formula, which may be the same as the simplest formula, or it may be each atom of the simplest formula multiplied by a certain number.

EXAMPLE.—A compound contains carbon, 92.31 per cent.; hydrogen, 7.69 per cent. One liter of its vapor at standard conditions weighs 3.482 grams. Find its correct formula.

First we find its simplest formula.

$$92.31 \div 12 = 7.69$$
  
 $7.69 \div 1 = 7.69$ 

The ratio of the number of carbon and hydrogen particles is 1 to 1. The simplest formula is CH.

If 1 liter of the vapor weighs 3.482 grams, then 22.4 liters will weigh 3.482 times 22.4, or 78 grams. The molecular weight is 78. But the molecular weight of CH is only 13, as we find by adding the atomic weights, carbon 12, and hydrogen 1. Therefore, each atom must be taken enough times to give the correct molecular weight, 78. By dividing 78 by 13, we find that each atom of the simplest formula must be taken 6 times. The correct formula is  $C_6H_6$ .

# SUMMARY

Gay-Lussac's law states that the combining volumes of gases and the volume of the product, if it be gaseous, may be expressed by small whole numbers.

Avogadro's theory assumes that equal volumes of all gases have the same number of molecules, the temperature and pressure being the same.

From Avogadro's theory it may be shown that the molecules of elementary gases contain 2 atoms.

One mole of a substance is its molecular weight times 1 gram.

To find the molecular weight of a volatile compound we find the weight in grams of 22.4 liters of its vapor at standard conditions of temperature and pressure. The weight in grams is numerically equal to the molecular weight.

A molar solution contains 1 mole of solute per 1000 grams of solvent. One mole of solute in 1000 grams of water lowers its freezing point 1.89°C. and raises its boiling point 0.52°C. The molecular weight of a substance may be found by determining the number of grams needed to produce such a change in the freezing point and boiling point of a solution.

## **OUESTIONS AND PROBLEMS**

- 1. Prove that the nitrogen molecule contains 2 atoms.
- 2. The molecular weight of hydrogen chlorid is 36.5. Find the weight of 1 liter of hydrogen chlorid in grams.
- 3. Find the weight of 1 liter of the following gases: CH<sub>4</sub>; H<sub>2</sub>N; C<sub>2</sub>H<sub>2</sub>; CO<sub>2</sub>; H<sub>2</sub>S. Could you find the weight of 1 liter of common table salt, NaCl, by the above method? Explain.
- 4. One liter of chlorin at standard conditions weighs 3.17 grams. Find its molecular weight.
- **5.** One liter of alcohol vapor weighs 1.592 grams at a temperature of 78°C. and under a pressure of 760 mm. of mercury. Find the molecular weight of alcohol.
- 6. At standard conditions 225 c.c. of sulfur dioxid weigh 0.6428 gram. Find the molecular weight of sulfur dioxid.
- 7. A compound contains oxygen, 69.49 per cent.; nitrogen, 30.51 per cent. Find its simplest formula. Find its molecular weight if 200 c.c. of the gas weigh 0.817 gram. Find the correct formula.

Reference Topics.—Gay-Lussac. Avogadro.

#### CHAPTER XIV

#### VALENCE

134. Valence Defined.—If we examine certain formulas, such as HCl, H<sub>2</sub>O, H<sub>3</sub>N, CH<sub>4</sub>, we observe that one hydrogen atom combines with one atom of chlorin to form hydrogen chlorid, HCl; two atoms of hydrogen combine with one of oxygen to form water, H<sub>2</sub>O; three atoms of hydrogen combine with one of nitrogen to form ammonia, H<sub>3</sub>N; and four hydrogen atoms are needed to combine with one carbon atom in marsh gas, CH<sub>4</sub>. The measure of the ability of the atom of one element to hold the atoms of other elements in combination is called its valence. Crudely, we may call valence the "grabbing power" of an atom.

135. Theory of Valence.—Just what the force is that holds one atom to another we do not know. Various chemists have used such expressions as "bonds" and "tubes of force" to represent chemical affinity. Very often the valence of elements is represented graphically as is shown below:

Each line or "bond" represents a valence of 1, and shows graphically that chlorin can hold 1 hydrogen atom; oxygen, 2; nitrogen, 3; and carbon, 4. The number of "bonds" an atom has tells us nothing concerning the stability of the

compounds it may form, but merely the number of atoms it does hold in that compound.

The modern theory of valence is that the force of attraction is electrical. J. J. Thomson suggests that certain elements, especially hydrogen and the metals, may lose one or more electrons, or negatively charged particles. Having thus lost an electron, they become positively charged, since taking away the negative leaves them positive. The nonmetals have the ability to take on one or more electrons, thus becoming charged negatively. To illustrate, 1 hydrogen atom carrying a positive charge will attract 1 chlorin atom which carries a negative charge. One oxygen atom carrying two negative charges attracts 2 hydrogen atoms each carrying one positive charge. The following graphic representation makes the theory clear:

136. Kinds of Valence.—The hydrogen atom never combines with more than 1 atom of any other element. Hence it is taken as the standard in valence. Hydrogen is said to be univalent. Chlorin is also univalent since 1 atom of chlorin combines with 1 atom of hydrogen. An element is said to be bivalent if its atom combines with two atoms of hydrogen or any other univalent element. The atom of a bivalent element has two "bonds," or its "grabbing power" is 2. Some elements are trivalent, having a valence of 3; elements whose valence is 4 are tetravalent; elements having a valence of 5 are pentavalent, and those whose valence is 6 are hexavalent. No element is known that has a valence of more than 8.

137. Valence of Binary Compounds.—If an element unites with hydrogen to form a binary compound we can

easily tell its valence. We learned that chlorin is univalent, since 1 atom of chlorin unites with 1 atom of hydrogen. One atom of oxygen holds 2 hydrogen atoms, therefore its valence is 2. In the same manner we learn that nitrogen has a valence of 3, and carbon a valence of 4.

Some elements do not readily combine with hydrogen, but such elements usually combine directly with oxygen. Examples are Na<sub>2</sub>O; CaO; Al<sub>2</sub>O<sub>3</sub>; SnO<sub>2</sub>. Since it takes 2 atoms of sodium to unite with 1 atom of bivalent oxygen, sodium must have a valence of 1. Similarly we conclude that calcium, Ca, is 2 since it unites with oxygen atom for atom. Aluminum, Al, is 3; and tin, Sn, is 4.

In any binary compound the product of the number of atoms of one element times its valence equals the product of the number of atoms of the other element times its valence. To illustrate, we may use the formula  $Al_2O_3$ . Showing the valence of each element by accent marks, as  $Al_2'''O_3''$ , we see at a glance that the products are equal, 3, the valence of aluminum, times 2, the number of aluminum atoms, being equal to 2, the valence of oxygen, times 3, the number of oxygen atoms.

Were the student to try to remember the formulas for so large a number of compounds as are treated in chemistry, the task would be stupendous. By learning the valence of the elements, he can readily determine the formula. Knowing that oxygen has a valence of 2, he should be able to write correctly the formula of any oxid, if he learns the valence of the other element. Copper has a valence of 2; therefore its oxid is CuO, not Cu<sub>2</sub>O<sub>3</sub>, nor CuO<sub>2</sub>. Since chlorin has a valence of 1, then sodium chlorid is NaCl; calcium chlorid is CaCl<sub>2</sub>; and aluminum chlorid is AlCl<sub>3</sub>.

138. Valence of Radicals.—It would seem as if the valence might be more difficult to determine in a compound containing three elements. This may be true, but usually

two of the elements form a radical. A radical is a group of elements that acts like a single element. In the compound sodium hydroxid, NaOH, the group (OH) is a radical. In sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, the (SO<sub>4</sub>) group is a radical. The compound nitric acid, HNO<sub>3</sub>, contains the radical (NO<sub>3</sub>). Since in a radical the two elements act like a single element, we can find the valence of a radical in exactly the same manner as we determined valence in binary compounds. For example the (OH) radical has a valence of 1; the (SO<sub>4</sub>) group has a valence of 2, since it unites with 2 atoms of hydrogen; the (NO<sub>3</sub>) group has a valence of 1.

Suppose we desire to write hydroxids of the metals whose valence we learned in paragraph 137. Calcium hydroxid is Ca(OH)<sub>2</sub>; aluminum hydroxid, Al(OH)<sub>3</sub>; and tin hydroxid, Sn(OH)<sub>4</sub>. For sulfates of these metals we write Na<sub>2</sub>SO<sub>4</sub>, CaSO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and Sn(SO<sub>4</sub>)<sub>2</sub>.

That the oxygen in a ternary compound usually holds in combination all the other elements may be seen from the following structural formulas:

$$Na - O - H$$
.  $H - O - N$ 
 $O$ 
 $H - O$ 
 $S$ 
 $O$ 

139. Variable Valence.—We have seen that some elements unite in different ratios and that such elements have more than one combining weight. Thus we would expect these elements to have more than one valence. The valence of some elements appears to be always the same, but some elements have a variable valence. Iron forms two oxids, one having the formula FeO; the other has the formula Fe<sub>2</sub>O<sub>3</sub>. The oxid in which iron has the lower valence is ferrous oxid; the other oxid is ferric oxid. Phosphorus also forms two oxids,  $P_2O_3$  and  $P_2O_5$ .  $P_2O_3$  is phosphorous oxid;  $P_2O_5$  is phosphoric oxid. Several elements have a variable valence. In variable valence, the

metallic element takes the ending ous for its lower valence compounds; the ending ic for the higher valence.

140. The Relation of Valence to Substitution.—Just as it is impossible to have 1 atom of a bivalent element combine with 1 atom of a univalent element, so do we find it impossible to substitute 1 bivalent atom for 1 univalent atom. When we try to substitute zinc for the hydrogen in sulfuric acid, 1 bivalent zinc atom takes the place of 2 hydrogen atoms. We may write the following equation:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$

With hydrogen chlorid we must use 2 molecules of HCl to furnish 2 hydrogen atoms.

$$Zn + 2HCl \rightarrow ZnCl_2 + \overset{\uparrow}{H}_2$$

141. Table of Valences.—To familiarize the student with the valences of the most common elements, a table is given here for use in the problems at the end of this chapter. The elements having a variable valence appear in two or more columns. In writing formulas it may help the beginner balance the compound if he writes after each element or radical an accent mark ('), to indicate its valence.

 $\textbf{Examples.} \textbf{--} \textbf{Ca''(CO_3)''; As_2'''S_3''; Mg''O''; P_2'''''O_5''}.$ 

Five One Two Four Six Al, Fe, N, C, Si, S, N. P  $\mathbf{S}$ Cl, H, I, Ca, Cu, Fe, Hg, Ag, Na, Mg, Hg, O, P Sn Sn, Zn, S

TABLE OF VALENCE

#### SUMMARY

The capacity of one atom of an element for holding 1 atom of hydrogen in combination is its valence.

In writing formulas of binary compounds the total number of bonds of one element must equal the number of bonds of the other element.

A radical is a group of elements that acts like a single element. Some elements have more than one valence.

## QUESTIONS .

1. In the top row of the following table certain elements and radicals are given with their valence indicated. In the left-hand column a number of metals are listed. Fill in the table for all the metals in the same manner as for the sodium compounds.

	Oxids O'' Na <sub>2</sub> O	Hy- droxids (OH)'	Chlorids Cl' NaCl	Nitrates (NO <sub>3</sub> )' NaNO <sub>3</sub>	Sulfates (SO <sub>4</sub> )" Na <sub>2</sub> (SO <sub>4</sub> )	Phosphates (PO4)"  Nas(PO4)	Carbonates (CO <sub>3</sub> )" Na <sub>2</sub> (CO <sub>3</sub> )
4							
'Na'							
κ΄							
Hg'							
Ag'							
Ca"							
Cu"							
Fe'''							
Mg"							
Al‴							
Pb"							
Fe"							
Zn"							
8n''''							

- 2. Write the formulas for the oxids of the following metals: K, Cu, Mg, Ag, and Zn.
- 3. Write two oxids for the following elements: Fe, Sn, Hg, N, and P.
- 4. Write the formulas for the hydroxids of all the elements given in question 1.
- 5. Write the formulas for two sulfates of the following: Fe, Sn, and Hg.

## CHAPTER XV

# CHEMICAL EQUATIONS

142. Equations.—Heretofore word equations have been used to represent the changes that take place during chemical reactions. The student is now able to understand equations using chemical formulas. Such equations have the advantage of being more brief and they show also more explicitly what occurs. A chemical equation is an algebraic expression used to represent a chemical reaction.

A chemical equation must be correct: (1) as to representation of facts; (2) as to valence; (3) as to algebra. Before an equation can be written one must know what substances enter into the reaction and what products are formed. For this knowledge we must rely upon experiment. Every compound in the equation must be balanced to see that each element has its correct valence. A molecule of each gaseous element should have 2 atoms. The third step is entirely mathematical; since no matter is lost during a chemical change, there must be the same number of atoms on one side of the equation as upon the other side.

143. Equations for Reactions Previously Studied.—The method of writing equations can be studied from some of the word equations that have been given. The equation for the preparation of oxygen by decomposing water is a very simple one. The substance used is water,  $H_2O$ ; the product formed are hydrogen,  $H_2$ , and oxygen,  $O_2$ . Thus we write,  $2H_2O \rightarrow 2H_2 + O_2$ . If we were to write  $H_2O \rightarrow H_2 + O$ , the equation would not be strictly correct, since the molecule of oxygen has 2 atoms.

We also prepared oxygen by heating potassium chlorate. The equation is as follows:

$$\uparrow 2KClO_3 \rightarrow 2KCl + 3O_2.$$

Let us now take up the study of an equation that is not quite so simple. When hydrogen chlorid is added to zinc, the zinc takes the place of the hydrogen which is set free. Zinc chlorid is the other product formed. If we write the equation as shown below,

$$Zn + HCl \rightarrow ZnCl + H$$
,

a little study shows that it is incorrect. It appears correct as to fact, but zinc is bivalent. Therefore zinc chlorid has the formula ZnCl<sub>2</sub>.

Writing the equation,

$$Zn + HCl \rightarrow ZnCl_2 + H$$
,

it appears correct as to fact and valence. It does not balance mathematically, since we have 2 chlorin atoms on the right side of the equation and but 1 on the left-hand side. We can not write  $HCl_2$  to remedy this defect without making hydrogen chlorid incorrect as to valence, but we can use 2 molecules of hydrogen chlorid. The equation,

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

is correct in every respect, fact, valence; and algebra. The student should always remember in writing equations that he may use as many molecules as are needed. He must check up the valence of each compound, and then balance the equation without interfering with valence.

The following equation is an example of metathesis:

It is customary in writing formulas to write the electropositive element first. This is usually either hydrogen or some metal. We would hardly expect two positive elements to unite chemically, nor two negative elements, since charges of like sign repel. In the above equation the silver (+) takes the place of the sodium (+), and unites with the chlorin (-); the sodium unites with the (NO<sub>2</sub>) radical, which is negative. We may be pretty certain that in double substitution a metallic element will be substituted for another metallic element and combine with a non-metal or a non-metallic radical. Radicals usually remain intact during chemical reactions. When a reaction is reversible the fact is indicated by use of the double arrow as in the following:

$$\uparrow 2HgO \rightleftharpoons 2Hg + O_2.$$

144. Problems Relating to Equations.—Weight.—Since chemical equations show the number of atoms taking part in a chemical reaction, the relative weights may be easily determined. In the equation,

$$2$$
HgO  $\rightarrow$  2Hg + O<sub>2</sub>,

we see that 2 molecules of mercuric oxid produce 2 atoms of mercury and 2 atoms of oxygen when decomposed. The approximate atomic weight of mercury is 200; and of oxygen, 16. Suppose we write these weights below the symbols in the equation, taking the weight of each atom as many times as that atom appears in the equation.

$$\begin{array}{ccc} 2 HgO \rightarrow & 2 Hg + O_{2} \\ 2 (200 + 16) & 2 (200) & 2 (16) \\ 432 & 400 & 32 \end{array}$$

It is evident from the above that if we heat 432 parts by weight of mercuric oxid, we obtain 400 parts by weight of mercury and 32 parts by weight of oxygen.

PROBLEM.—How many grams of oxygen may be obtained by heating 30 grams of mercuric oxid?

Solution.—Since 32/432 of mercuric oxid is oxygen, from 30 grams we can obtain as many grams of oxygen as 32/432 of 30 grams. The result is 2.22 grams. The problem may be solved by simple proportion:

Total molecular weight: molecular weight of oxygen = total number of grams: number of grams of oxygen. Or, 432:32 = 30:x.

$$x = 2.22$$
 grams.

Problem.—How many grams of potassium chlorate must be used to prepare 40 grams of oxygen?

SOLUTION.—Let us first write the equation with the atomic weights.

To obtain 96 grams of oxygen, 245 grams of potassium chlorate are needed. To prepare 40 grams of oxygen, we need 245/96 of 40 grams, or 102.08 grams of potassium chlorate.

By proportion, 96:245 = 40:x.

$$x = 102.08 \text{ grams.}$$

PROBLEM.—How many grams of hydrogen will be liberated by the action of 100 grams of zinc on sulfuric acid? How many liters will the hydrogen occupy at standard conditions?

Solution.—
$$Z_n$$
 +  $H_2SO_4$   $\longrightarrow$   $Z_nSO_4$  +  $H_2$  65 (2 + 32 + 64) (65 + 32 + 64) 2 65 98 161 2.

From the equation we see that 65 grams of zinc liberate 2 grams of hydrogen. 100 grams of zinc will liberate 100/65 of 2 grams, or 3.08 grams. By proportion, 65:100 = 2:x. Whence x = 3.08 grams.

Since 1 liter of hydrogen weighs 0.09 gram, 3.08 grams will occupy as many liters as  $3.08 \div 0.09$ . The answer is 34.2 liters.

145. Problems Relating to Equations.—Volumes.—In dealing with solids and liquids weight relations are used as in the preceding paragraph. With gases, the work may be shortened by using Avogadro's theory and the law of Gay-Lussac.

Problem.—How many liters of oxygen will be required for the combustion of 14 liters of hydrogen?

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$
.

We know that the combining volumes of gases have the same ratio as the number of molecules. If 2 volumes of hydrogen combine with 1 volume of oxygen, 7 volumes of oxygen will be needed to combine with 14 volumes of hydrogen. The answer is 7 liters of oxygen.

PROBLEM.—How many liters of oxygen are needed for the complete combustion of 10 liters of marsh gas, CH<sub>4</sub>?

EQUATION.—
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
.

One mole of marsh gas combines with 2 moles of oxygen to form 1 mole of carbon dioxid and 2 moles of water vapor. By Avogadro's theory, 2 volumes of oxygen unite with 1 volume of CH<sub>4</sub>. For 10 liters of CH<sub>4</sub>, 20 liters of oxygen are needed.

# EQUATIONS

(For reference here and use in solving problems; to be studied during the review in place of word equations.)

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2.$$

$$\downarrow \qquad \qquad \downarrow$$

$$CaCO_2 + H_2O + CO_2 \rightleftarrows CaH_2(CO_3)_2.$$

$$H_4NCl + NaNO_2 \rightarrow NaCl + H_4N NO_2$$

$$\downarrow \qquad \qquad \uparrow$$

$$2H_2O + N_2.$$

### **QUESTIONS AND PROBLEMS**

- 1. How many grams of oxygen can be prepared from 20 grams of potassium chlorate?
- 2. How many grams of oxygen can be prepared from 20 grams of mercuric oxid?
- 3. If mercuric oxid and potassium chlorate were the same price per pound, which would you use for preparing oxygen? Explain.
- 4. How many grams of zinc are needed to liberate 2 liters of hydrogen from sulfuric acid?
- 5. How many liters of oxygen will be needed for the complete combustion of 2 liters of carbon monoxid?
- 6. The burning of acetylene may be represented by the following equation:

$$\uparrow$$
 2C<sub>2</sub>H<sub>2</sub> + 5O<sub>2</sub>  $\rightarrow$  4CO<sub>2</sub> + 2H<sub>2</sub>O.

When 5 liters of acetylene burn, find the volume of the oxygen used and the volume of carbon dioxid that is formed.

7. Using the following equation, find how many pounds of hydrogen chlorid are required to unite with 10 lbs. of iron:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$
.

How many pounds of ferrous chlorid are produced?

- 8. If 100 grams of zinc are treated with 120 grams of sulfuric acid, which will remain, zinc or acid, and how many grams?
- 9. How many pounds of copper can be obtained from 50 lbs. of copper oxid? How many pounds of copper sulfate can be made from this copper?
- 10. How many grams of potassium chlorate are needed to prepare 6 moles of oxygen? To prepare 22.4 liters of oxygen?

# CHAPTER XVI

# ACIDS, BASES, AND SALTS

- 146. Acids, Bases, and Salts.—Of the many compounds studied in chemistry, a large number belong to one of three classes: acids, bases, and salts. In this chapter the general characteristics of each class will be studied, exemplified by some of the most common representatives.
- 147. Acids.—At the ordinary temperature some acids are gaseous, some liquid, and others solid. For example, hydrogen chlorid is a gas; nitric acid and sulfuric acid are liquids; tartaric, boric, and oxalic acids are solids. While acids have no physical properties in common, yet in water solution they have many chemical properties that are characteristic. Since the pure acid does not have these characteristics, the name acid usually refers to a dilute or concentrated solution of the acid in water. For example, concentrated nitric acid is a water solution, 68 per cent. nitric acid to 32 per cent. water. Ordinary concentrated sulfuric acid is about 93.5 per cent. sulfuric acid.
- 148. General Characteristics of Acids.—Several characteristics are common to all acids: (1) they contain hydrogen; (2) they have a sour taste; (3) they change the color of certain substances known as indicators; thus acids change the color of litmus from blue to red; (4) they neutralize bases forming salts and water; (5) they act on certain metals forming salts and liberating hydrogen; (6) they act on oxids of metals forming salts and water.
- 149. Preparation of Acids.—When we studied the chemical properties of water we found that it would unite with

the oxids of non-metals to form acids. For example, SO<sub>2</sub>, the oxid of the non-metal sulfur, unites with water to form sulfuric acid, H<sub>2</sub>SO<sub>4</sub>.

$$H_2O + SO_3 \rightleftharpoons H_2SO_4$$
.

The oxid of a non-metal that unites with water to form an acid is called an acid anhydrid. The above equation is reversible. When sulfuric acid is rendered anhydrous by removing the water, the acid anhydrid remains. Nitrogen pentoxide,  $N_2O_5$ , is the anhydrid of nitric acid as the following equation shows:  $N_2O_5 + \frac{1}{2}H_2O \rightleftharpoons 2HNO_3$ .

In the manufacture of most acids, however, an entirely different method of preparation is used. Suppose we desire to prepare nitric acid; it contains hydrogen and the NO<sub>3</sub> radical. Sodium nitrate, NaNO<sub>3</sub>, a compound found extensively in Chile contains the same radical. By heating this compound with sulfuric acid metathesis occurs as represented by the following equation:

$$2\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HNO}_3.$$

Hydrogen chloride is prepared in an analogous manner from sodium chlorid.

$$\uparrow
2NaCl + H2SO4 \rightarrow Na2SO4 + 2HCl.$$

The gas that is driven off is dissolved in water and sold under the name hydrochloric acid.

Most acids are prepared by heating a compound containing the acid radical or acid forming element with sulfuric acid. Sulfuric acid is used in preparing other acids for three reasons: (1) it has a very high boiling point; (2) it is one of the cheapest acids: (3) it is fairly stable.

150. Naming of Acids.—Acids that are made up of two elements only are named as other binary compounds. HCl is hydrogen chlorid; unfortunately its water solution is



Sir Humphrey Davy (1778-1829) was an English chemist and philosopher. He studied electrolysis, and by passing an electric current substances through fused discovered solutions. and several elements, including sodium, potassium, strontium, and magnesium. Davy discovered that nitrous oxid is an anesthetic. He proved that chlorin is an element. and showed that hydrogen chlorid is composed of hydrogen and chlorin. He is well-known as the inventor of the miner's safety lamp. In 1820 he was made president of the Royal Society of England.

Johann Jacob Berzelius (1779-1848) was a Swedish chemist. His work in analytical chemistry was so accurate that he discovered several elements, including cerium, selenium, and tho-He determined the rium. equivalent weight of many elements and improved ana-He was lytical methods. the originator of the system of symbols used in chemistry.





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called hydrochloric acid. The beginner in chemistry is sometimes confused because of this irregularity. Other examples of acids that contain two elements only are hydrogen bromid, HBr, and hydrogen sulfid, H<sub>2</sub>S.

We have learned that all acids contain hydrogen. all acids also contain oxygen. The method of naming acids that contain oxygen is not so simple since the same acid For example, forming element often forms a series of acids. the following oxygen acids of chlorin are known: HClO4, HClO<sub>3</sub>, HClO<sub>2</sub>, and HClO. Since they all contain chlorin the root "chlor" is used in all cases. The most common of the oxygen acids takes the ending ic. For example, HClO<sub>3</sub>, the most common oxugen acid of chlorin, is called chlor-ic The acid containing less oxygen than the ic acid takes the ending ous. Thus chlor-ous acid is HClO<sub>2</sub>. The same ending is used for the acid containing still less oxygen than the ous acid, but the Greek prefix hypo (under) HClO is the formula for hypo-chlor-ous acid. is used. The acid containing more oxygen than the ic acid takes the ending ic, but the Latin prefix per (thoroughly saturated with) is used. The formula for per-chloric acid is HClO<sub>4</sub>.

- 151. Bases.—The following bases are the most common: sodium hydroxid, potassium hydroxid, ammonium hydroxid (aqua ammonia), and calcium hydroxid. Sodium hydroxid and potassium hydroxid are white deliquescent solids, very soluble in water. Ammonium hydroxid is a compound formed by dissolving ammonia gas in water. Calcium hydroxid is slightly soluble in water. Its water solution is known as lime-water. The soluble bases that have the characteristics of strong bases given in the following paragraph are called alkalis.
- 152. Characteristics of Soluble Bases.—(1) Bases contain one or more hydroxyl (OH) groups; (2) they have a bitter taste; (3) they also affect indicators; they turn red litmus blue; (4) they neutralize acids forming salts and water; (5)

they have a slippery feeling in solution; (6) they act corrosively on the flesh, especially on fats to form soaps.

153. Preparation of Bases.—1. Such active metals as sodium and potassium interact with water to form bases; hydrogen gas is liberated. Calcium acts on water slowly forming calcium hydroxid, a base. The equations are as follows:

$$2Na + 2H2O \rightarrow 2NaOH + H2$$

$$2K + 2H2O \rightarrow 2KOH + H2$$

$$\uparrow$$

$$Ca + 2H2O \rightarrow Ca(OH)2 + H2$$

2. The oxids of some metals unite with water to form bases. The oxid of a metal that unites with water to form a base is called a basic anhydrid. The following reversible equation shows the action between calcium oxid, a basic anhydrid, and water.

$$CaO + H_2O \rightleftharpoons Ca(OH)_2$$
.

Insoluble bases are prepared by adding to the solution of a compound containing the metal some soluble base. Metathesis occurs, the insoluble base being precipitated. In the following equation the insoluble base is ferric hydroxid.

$$\mathrm{FeCl_3} + 3\mathrm{NaOH} \rightarrow \mathrm{Fe(OH)_3} + 3\mathrm{NaCl.}$$

154. Nomenclature of Bases.—The method of naming bases is extremely simple. They take the name of the metal from which they are formed followed by the word hydroxid. Formerly they were called hydrates and the name is still used occasionally. Because they act so readily on the skin and flesh, sodium hydroxid and potassium hydroxid are often called caustic soda and caustic potash respectively.

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155. Neutralization.—If we add 1 mole of sodium hydroxid in solution to 1 mole of hydrochloric acid, neutralization occurs as represented by the following equation:

$$NaOH + HCl \rightarrow NaCl + H_2O$$
.

The solution that is formed affects neither blue nor red litmus. It does not have any of the characteristic properties of either the base or the acid. We say the solution is neutral. If we evaporate the solution, water is driven off and sodium chlorid, a salt, remains as a crystalline solid. Neutralization is the name given to the process that occurs when an acid and a base are brought together in such proportions that each destroys the properties of the other. A salt and water are the products formed.

156. Salts.—The properties of salts are so widely divergent that it is almost impossible to give any general properties. They are usually crystalline solids. Their color varies; the majority are white, but cobalt salts are pink, copper salts are blue, and nickel and ferrous iron salts are green.

Salts may be prepared in several ways. Often the same salt may be prepared by four or five different methods. Some of the methods are outlined here briefly with one or two examples to illustrate each method.

1. By the Direct Union of the Elements.

Example.—
$$2Na + Cl_2 \rightarrow 2NaCl$$
.

2. The Interaction of an Acid and a Metal.

EXAMPLES.—2Na + 2HCl 
$$\rightarrow$$
 2NaCl + H<sub>2</sub>.

$$\uparrow$$

$$Zn + H2SO4  $\rightarrow$  ZnSO<sub>4</sub> + H<sub>2</sub>.$$

3. The Action of an Acid on the Oxid of a Metal.

Examples.—Na<sub>2</sub>O + 2HCl 
$$\rightarrow$$
 2NaCl + H<sub>2</sub>O.

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$
.

- 4. Neutralization.—Examples were given in the preceding paragraph.
- 5. Metathesis.—This is a very useful method of preparing salts since two salts are often prepared during one reaction. Upon mixing solutions of silver nitrate and sodium chlorid, as in the following equation,

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$
,

the silver chlorid which is insoluble may be removed by filtration and the soluble sodium nitrate recovered by evaporating the water which was present.

157. Naming of Salts.—Since a salt is really composed of the metal of a base and an acid-forming element, or an acid radical, it is named from both base and acid. Salts take the name of the metal of the base from which they were formed, use the root and prefix of the acid, but change the ending ic to ate and the ending ous to ite. The following table illustrates the method of naming the salts that are formed when sodium hydroxid neutralizes the chlorin acids discussed in paragraph 150.

	ACIDS		SALTS	
HClO <sub>4</sub>	per-chlor-ic	NaClO <sub>4</sub>	sodium	per-chlor-ate
HClO <sub>3</sub>	chlor-ic	NaClO <sub>3</sub>	sodium	chlor-ate
HClO <sub>2</sub>	chlor-ous	NaClO <sub>2</sub>	sodium	chlor-ite
HClO	hypo-chlor-ous	NaClO	sodium	hypo-chlor-ite
HCl	hydrogen chlorid, or	NaCl	sodium	chlor-id.
	hydrochloric			

### SUMMARY

All acids contain hydrogen; they have a sour taste, turn blue litmus red, act on metals forming a salt and hydrogen, act on oxids of metals forming a salt and water, and neutralize bases. The oxid of a non-metal that unites with water to form an acid is called an acid anhydrid. Acids are generally prepared by the action of sulfuric acid on a salt that contains the acid-forming element or group of elements.

The most common acid containing oxygen has the ending ic. An acid in the same series containing less oxygen has the ending ous. When an acid has still less oxygen than the ous acid in the series, it takes the ending ous, but uses the prefix hypo. An acid having more oxygen than the ic acid takes the ic ending and uses the prefix per.

Bases contain one or more hydroxyl groups; they have a bitter taste, turn red litmus blue, and neutralize acids. Soluble bases have a slippery feeling and readily saponify fats to form soaps.

Bases are prepared by the action of a metal or the oxic of a metal on water.

When a base is added to an acid the properties of both are destroyed. The process is called neutralization. Water and a salt are formed.

Salts may be prepared in several ways: (1) synthesis; (2) neutralization; (3) action of an acid on a metal; (4) action of an acid on the oxid of a metal; (5) double decomposition.

Salts take the name of the metal of the base from which they are formed, use the same root and prefix as the acid, and change the acid ending ic to ate; the ending ous to ite.

# QUESTIONS AND PROBLEMS

- 1. Of what acid is CO<sub>2</sub> the anhydrid? SO<sub>2</sub>? N<sub>2</sub>O<sub>3</sub>? P<sub>2</sub>O<sub>5</sub>?
- 2. From the rules for naming salts what ending would you expect a salt formed from hydrochloric acid to have? What is the correct ending? Why?
- 3. Phosphoric acid has the formula  $H_3PO_4$ . Write the formula for phosphorous acid. For hypophosphorous acid.
  - 4. The following acids have the ending ic. Write the formulas

and names for as many other acids in the series as possible. HNO<sub>2</sub>; HIO<sub>2</sub>; HBrO<sub>2</sub>; H<sub>2</sub>SO<sub>4</sub>.

- 5. Balance and complete the following neutralization equations:
- (a) NaOH +  $H_2SO_4 \rightarrow$
- (b) NaOH +  $H_2PO_4 \rightarrow$
- (c)  $Ca(OH)_2 + H_2SO_4 \rightarrow$
- (d)  $Ca(OH)_2 + HCl \rightarrow$
- (e)  $Ca(OH)_2 + H_2PO_4 \rightarrow$
- $(f) \text{ Al(OH)}_3 + \text{H}_2\text{SO}_4 \rightarrow$
- 6. Give the correct names for all the salts formed in the preceding equations.
- 7. Devise three methods of forming the salt potassium chlorid, KCl. Three methods of preparing calcium nitrate Ca(NO<sub>3</sub>)<sub>2</sub>.
- 8. Name as many foods as you can that contain acids. How would you verify your conclusion?
- 9. If sodium hydroxid and potassium hydroxid were the same price per pound which would you use as a base? Explain.
- 10. Which one of the bases mentioned in paragraph 151 would you use to clean a greasy sink? To remove grease spots from rugs or clothing? To neutralize acid stains on clothing?
- 11. How many grams of sodium hydroxid will be required to neutralize 85 grams of hydrogen chlorid?
- 12. How many moles of sodium hydroxid will be required to neutralize 1 mole of hydrochloric acid? One mole of sulfuric acid? One mole of phosphoric acid?

### CHAPTER XVII

## AMMONIA AND AMMONIUM COMPOUNDS

158. Occurrence of Ammonia.—Traces of ammonia are found in the air from the decay of plants and animals. As it dissolves in the rain water it finds its way into the soil.

159. Preparation.—1. Laboratory.—Ammonia is pre-

pared in the laboratory by heating a mixture of ammonium chlorid and calcium hydroxid. The gas is collected by air displacement (see Fig. 55). In the equation,

$$2H_4NCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_4NOH,$$

the (H<sub>4</sub>N) group acts like a positive radical and takes the place of calcium by substitution. the compound H<sub>4</sub>NOH is unstable, the heat of the reaction breaks it up into ammonia, H<sub>3</sub>N, and water.

$$H_4NOH \rightleftharpoons H_3N + H_2O.$$

· When sodium hydroxid is used instead of calcium hydroxid to prepare ammonia, the reaction is as follows:

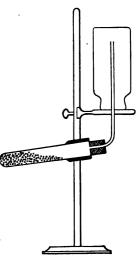


Fig. 55.—Apparatus for preparing ammonia.

$$H_4NCl + NaOH \rightarrow NaCl + H_4NOH$$

$$\downarrow \uparrow$$

$$H_3N + H_2O.$$

- 2. Commercial Preparation.—When coal is heated in retorts to prepare illuminating gas, ammonia is given off as a by-product. The ammonia dissolves in the water with which the coal gas is washed. This impure solution is treated with lime and heated to drive off the ammonia which is re-dissolved in pure water. Such a solution forms the aqua ammonia of commerce.
- 3. Direct Union of the Elements.—We learned that nitrogen combines with hydrogen to form ammonia when an electric spark is passed through a mixture of the two gases. The equation is one of simple combination:

$$\uparrow 
N2 + 3H2  $\rightleftharpoons$  2H<sub>3</sub>N.$$

Haber found that hydrogen and nitrogen under high temperature and pressure unite readily to form ammonia in the presence of a suitable catalytic agent, such as finely divided iron. Large plants have been constructed in Germany to make ammonia by this process for use as fertilizers.

160. Physical Properties of Ammonia.—Ammonia is a gaseous compound having the formula H₃N. It has a peculiar, pungent odor and a bitter taste. Ammonia is lighter than air and very soluble in water. One liter of water at 20°C. dissolves 710 liters of ammonia gas. At 0°C. 1 liter of water dissolves more than 1100 liters of the gas. The very high solubility is probably due to a chemical union between the gas and water to form ammonium hydroxid.

The ammonia water thus formed is lighter than water, the specific weight of the 35 per cent. solution being 0.88. When ammonia water is boiled the gas is all driven off Even under ordinary atmospheric pressure ammonia gas condenses to a liquid when sufficiently cooled. Its boiling point is  $-34^{\circ}$ C. Liquid ammonia is put on the market compressed in steel cylinders.

161. Chemical Properties.—Ammonia neither burns nor supports combustion. In oxygen, however, it burns slowly. Heated with copper oxid, it forms water and nitrogen.

When ammonia dissolves in water it unites with the water according to the equation,

$$H_3N + H_2O \rightleftharpoons H_4N OH.$$

The (H<sub>4</sub>N) group is a radical. Since the OH group is present and the water solution acts like a base, this radical acts like a metal. It is called the ammonium radical. Students should be careful not to confuse the gas ammonia, H<sub>3</sub>N, with the hypothetical metal or ammonium radical, H<sub>4</sub>N. In ammonia the valence of nitrogen is 3; in the ammonium radical, it is 5. A water solution of ammonia or the moist gas combines readily with acids, forming salts by neutralization. For example,

$$H_4NOH + HCl \rightarrow H_4NCl + H_2O.$$
  
2 $H_4NOH + H_2SO_4 \rightarrow (H_4N)_2SO_4 + 2H_2O.$ 

- 162. Uses of Ammonia.—1. As a Fertilizer.—The importance of ammonia and ammonium compounds as fertilizers was discussed under nitrogen.
- 2. As a Detergent.—Since aqua ammonia is a base we would expect it to act upon fats and oils. It is quite extensively used in the household for removing grease spots. Since the gas is liberated as soon as the water evaporates, it does not injure the fabric as do such bases as sodium and potassium hydroxid. It may dissolve the dye in a colored fabric, however.
- 3. For Refrigeration.—If we pour water on one hand and let it evaporate quickly, the hand is cooled. It requires heat to convert water into its vapor. In the illustration, the heat came from the hand, thus producing the cooling effect. If we use alcohol instead of water the cooling effect.

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is more marked, since the alcohol evaporates more rapidly. This principle of cooling by evaporation is used in making ice, the water losing so much heat that it solidifies. Since alcohol, boiling at 78°C. produces a more marked cooling effect than water, boiling at  $100^{\circ}$ C., we would expect liquid ammonia, which boils at  $-34^{\circ}$ C., to take in heat very rapidly upon evaporation. This is especially true since liquid ammonia has quite a high heat of vaporization, about 295 calories of heat being needed to convert 1 gram of liquid ammonia into ammonia gas.

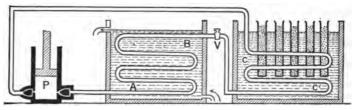


Fig. 56.—Diagram of an artificial ice plant.

Fig. 56 shows how the principle is applied. By using a compression pump P, ammonia gas is liquefied in the pipes, A-B, around which cold water flows to absorb the heat liberated as the gas liquefies. The liquid ammonia passes through an expansion valve, V, into a series of coils, C-C', which are immersed in brine. As the ammonia in the coils evaporates heat is absorbed until the brine is cooled below the freezing point of fresh water. Cans of fresh water immersed in the brine are frozen after several hours into cakes of solid ice.

In cold storage plants the cold brine is pumped through pipes in the storage room. Just as hot water flowing through pipes in a room warms it by radiation, so the circulation of cold brine cools the room and keeps it at any desired temperature.

#### SUMMARY

Ammonia is formed by the decay of animal and vegetable matter. It is prepared in the laboratory by heating a mixture of calcium hydroxid and ammonium chlorid. The chief commercial source is from the distillation of coal. Ammonia may be prepared from the elements by using a catalytic agent or an electric spark to facilitate composition.

Ammonia is a colorless gas; it may be recognized by its peculiar odor; it is very soluble in water.

Ammonia neither burns nor supports combustion. Its water solution forms a base called ammonium hydroxid. In this base the  $H_4N$  radical acts like a metal.

Ammonia is used (1) as a fertilizer; (2) as a detergent; and (3) for making artificial ice.

### **QUESTIONS AND PROBLEMS**

- 1. Dry ammonia gas does not affect litmus paper. Explain.
- 2. Gases are often dried by bubbling them through concentrated sulfuric acid. Could ammonia be dried in this manner? Explain.
  - 3. Why is ammonia called the volatile alkali?
  - 4. What is meant by the ammonium theory?
- 5. Write the equation to show the interaction between ammonium hydroxid and nitric acid.
- 6. How many grams of ammonia can be prepared from 40 grams of ammonium chlorid? How many liters?
- 7. How many grams of ammonium chlorid would be required to prepare 20 liters of ammonia?

Topic for Reference.—Cold storage plants.

### CHAPTER XVIII

## NITRIC ACID AND THE OXIDS OF NITROGEN

# 163. Preparation of Nitric Acid.—(a) Laboratory.—In

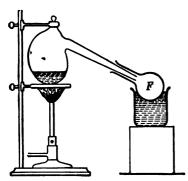


Fig. 57.—Preparation of nitric acid.

the laboratory nitric acid is prepared by the general method outlined in paragraph 149. A nitrate, usually sodium nitrate, is heated in a retort with an excess of sulfuric acid (see Fig. 57). The nitric acid volatilizes and is then condensed in the tube of the retort and in the receiver F. Two equations are possible since different re-

actions occur when the relative amounts of acid and salt are varied.

(a) 
$$NaNO_3 + H_2SO_4 \rightarrow HNaSO_4 + HNO_3$$
.

(b) 
$$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3$$
.

Since less heat is required when only half enough sodium nitrate is used to neutralize the sulfuric acid, as shown in equation (a), these proportions are usually used. The higher temperature needed for the latter reaction decomposes some of the nitric acid.

(b) Commercial.—The commercial method is the same 154

as the laboratory method, the mixture being heated in iron retorts.

Some nitric acid is now being made synthetically as discussed in paragraph 113.

- 164. Properties of Nitric Acid.—(a) Physical.—Nitric acid is a colorless oily liquid, more than 1½ times as heavy as water. The pure acid boils at 86°C. It fumes in moist air. Since the pure acid is unstable, the concentrated nitric acid of commerce is a water solution containing 68 per cent. nitric acid. Such a solution boils at 120°C. A more dilute solution boils at a lower temperature and loses water thus becoming more concentrated.
- (b) Chemical.—1. Acid Action.—Nitric acid is a very strong acid, acting on oxids of metals to form nitrates. It neutralizes bases. Its acid properties are more marked in dilute water solution.
- 2. Stability.—When boiled or exposed to sunlight, nitric acid decomposes, forming water, oxygen, and nitrogen tetroxid.

$$\uparrow \qquad \uparrow \qquad \uparrow \qquad \uparrow \qquad 4HNO_3 \rightarrow 2H_2O + 4NO_2 + O_2.$$

The acid is more stable in water solution. When the concentrated acid decomposes, part of the nitrogen tetroxid dissolves in the acid imparting to it a yellow color. Nitric acid containing a large quantity of the tetroxid in solution is red in color. It is known as fuming nitric acid. Phosphorus pentoxid dehydrates nitric acid, leaving nitric anhydrid,  $N_2O_5$ , a white crystalline solid.

$$P_2O_5 + 2HNO_3 \rightarrow N_2O_5 + 2HPO_3$$
.

3. Oxidizing Action.—In the presence of a reducing agent, nitric acid may decompose as follows:

$$\uparrow$$
  $\uparrow$   $\uparrow$  2HNO<sub>3</sub> $\rightarrow$ H<sub>2</sub>O + 2NO + 3(O).

Since the oxygen is in the nascent state, nitric acid acts as a strong oxidizing agent. It readily oxidizes organic matter, such as hair, wool, and vegetable fibers. When charcoal is heated red hot and thrust into nitric acid it burns vigorously, the oxygen needed for combustion coming from the nitric acid. The products formed when the acid is reduced are very numerous. A partial reduction may occur, resulting in the formation of the various oxids of nitrogen, or the acid may be more completely reduced to form ammonia. Nitric acid stains the skin and proteins a bright yellow, forming xantho-proteic acid. This action may be used to test for proteins.

4. Action with Metals.—Because nitric acid is a good oxidizing agent even in rather dilute solution, it seldom liberates hydrogen when it interacts with a metal. Only when the metal is very active and the acid very dilute do such reactions as the following occur:

The fairly concentrated acid acts upon such metals as copper forming a nitrate, water, and nitric oxid, NO. We may write the equation in three steps as follows:

$$2HNO_{3}\rightarrow H_{2}O + 2NO + 3(O) \\ \downarrow \\ 3Cu + 3(O)\rightarrow 3CuO \\ \downarrow \\ \hline \\ 3CuO + 6HNO_{3}\rightarrow 3Cu(NO_{3})_{2} + 3H_{2}O.$$

All the above equations may be combined into one.

$$\uparrow$$
 3Cu + 8HNO<sub>3</sub> $\rightarrow$ 3Cu(NO<sub>3</sub>)<sub>2</sub> + 4H<sub>2</sub>O + 2NO.

Unfortunately it is quite impossible to determine the intermediate steps that occur during a chemical reaction.

The final products can be accurately determined. Probably the nascent oxygen formed when nitric acid decomposes, oxidizes the copper to copper oxid; the oxid later dissolving in the excess acid forming water and copper nitrate. Nitric acid does not act upon gold and platinum and only slightly upon aluminum. It attacks all other common metals.

165. Uses of Nitric Acid.—1. Preparation of Nitrates.—
Nitrates are salts of nitric acid; they are formed when nitric acid acts upon metals or metallic oxids, sodium nitrate being the only one that occurs extensively in nature.

All nitrates are readily soluble in water. Sodium, potassium, and calcium nitrates are the most important representatives of this class of salts. They find extensive use in fertilizers and in making explosives. When heated, sodium and potassium nitrate lose one atom of oxygen and form nitrites.

$$\uparrow$$
 2NaNO<sub>3</sub>  $\rightarrow$  2NaNO<sub>2</sub> + O<sub>2</sub>.

With the exception of ammonium nitrate, other nitrates decompose as follows when heated:

$$\begin{array}{c} \uparrow & \uparrow \\ 2\text{Pb}(\text{NO}_3)_2 \rightarrow 2\text{PbO} + 4\text{NO}_2 + \text{O}_2. \end{array}$$

- 2. In Dye Industry.—Nitric acid is used for making aniline, which is the starting point for a large number of basic dyes.
- 3. Making Explosives.—Glycerin is a thick oily liquid obtained as a by-product in the manufacture of soap. Its formula is  $C_3H_5(OH)_3$ . Concentrated nitric acid acts upon it forming glyceryl nitrate, or nitro-glycerin. The equation is as follows:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O.$$

Concentrated sulfuric acid is used with the nitric acid

in such reactions to absorb the water that is formed, thus preventing the dilution of the nitric acid. Nitro-glycerin is a heavy oily liquid. It burns readily. Since 1 molecule has more than enough oxygen to combine with all its carbon and hydrogen, it burns without access to air forming water vapor, carbon dioxid, nitrogen, and oxygen. Since these gases occupy many times the volume of the nitro-glycerin, enormous pressure is produced by such decomposition. Such compounds as nitro-glycerin are said to explode by detonation.

Infusorial earth consists of the microscopic skeletons of an order of one-celled animals. It absorbs from 40 to 75 per cent. of nitro-glycerin forming *dynamite*. Dynamite is a safer explosive to handle than the liquid nitro-glycerin.

Cotton fibers consist of nearly pure cellulose, (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>. When nitric acid acts on cellulose a series of nitrates is formed. Concentrated nitric acid with sulfuric yields cellulose hexa-nitrate, or gun-cotton. More dilute acid gives di-, tri-, tetra-, or penta-nitrate of cellulose, which are less powerful explosives. Cellulose hexa-nitrate has the formula,  $C_{12}H_{14}O_4(NO_3)_6$ . With ether it does not dissolve but forms a plastic colloidal suspension that may be pressed into various shapes and cut into different-sized grains of smokeless powder. When it explodes, carbon monoxid, carbon dioxid, water vapor, and nitrogen are formed. As these substances are all gases no smoke is produced. This powder is also superior to the old black gunpowder because it is more powerful, thus making a gun in which it is used more efficient with a smaller weight of ammunition. Blasting gelatin is an exceedingly powerful explosive made from nitroglycerin and collodion. Collodion is an alcohol and ether solution of a mixture of the lower cellulose nitrates. used in surgery as liquid court plaster; it also finds use in photography. Celluloid is formed by treating cellulose nitrates with camphor. The cellulose nitrates are often incorrectly called nitro-celluloses. In exploding them it is customary to use a *detonator*. Fulminate of mercury, HgC<sub>2</sub>N<sub>2</sub>O<sub>2</sub>, is put in a cap and as it explodes violently by a sudden shock, it in turn explodes the powders by detonation (Fig. 58).

Tri-nitro-toluol (T.N.T.) is another explosive that is made by using nitric acid. Toluol, C<sub>7</sub>H<sub>8</sub>, a coal-tar prod-

uct, is treated with a mixture of nitric and sulfuric acids, the tri-nitro-toluol being formed. It has the formula  $C_7H_5(NO_2)_3$ .

Picric acid is a yellow crystalline solid that is made by the action of nitric acid on phenol, or carbolic acid, C<sub>6</sub>H<sub>5</sub>OH. Its formula is C<sub>6</sub>H<sub>2</sub>OH(NO<sub>2</sub>)<sub>3</sub>; it is trinitro-phenol. Picric acid and its salts are violently explosive.

166. Nitrous Acid and Nitrites.—We have seen that the nitrates of sodium and potassium lose 1 atom of oxygen when heated, forming the nitrites, NaNO<sub>2</sub> and KNO<sub>2</sub>. When sodium nitrite in dilute solution is treated with an acid, nitrous acid is formed.

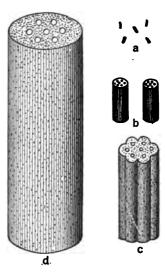


Fig. 58.—Grains of smokeless powder. a. Rifle powder. b. For 3-in. gun. c. For 6-in. gun. d. For 12-in. gun. (Actual size).

The acid is unstable, decomposing into water, nitric acid, and nitric oxid, NO. It is used extensively in making certain dye-stuffs. Nitrogen trioxid,  $N_2O_3$ , is its anhydrid.

$$N_2O_3 + H_2O \rightarrow 2HNO_2$$

167. Oxids of Nitrogen.—The valence of nitrogen is so varied that it is possible for the element to form five oxids.

Nitrogen monoxid, or nitrous oxid, has the formula N<sub>2</sub>O; nitrogen dioxid, or nitric oxid, has the formula NO, or N<sub>2</sub>O<sub>2</sub>; nitrogen trioxid, or nitrous anhydrid, has the formula N<sub>2</sub>O<sub>3</sub>; nitrogen tetroxid, commonly called nitrogen peroxid, has the formula NO<sub>2</sub>, or N<sub>2</sub>O<sub>4</sub>; nitrogen pentoxid, or nitric anhydrid, has the formula N<sub>2</sub>O<sub>5</sub>. The anhydrids of nitrous and nitric acids have already been discussed. They are useful oxidizing agents.

168. Nitrous Oxid.—(a) Preparation.—Nitrous oxid is prepared by heating ammonium nitrate.

$$H_4NNO_3 \rightarrow 2H_2O + N_2O.$$

- (b) Physical Properties.—Nitrous oxid is a colorless gas with a sweetish odor and taste. It is heavier than air and moderately soluble in water. It may be easily condensed to a liquid, in which form it is usually put on the market.
- (c) Chemical Properties.—At ordinary temperatures this gas is stable but at increased temperatures it decomposes into nitrogen and oxygen. Since the mixture (2 to 1) of gases thus formed is richer in oxygen than the air (4 to 1), nitrous oxid supports combustion better than air. A glowing splinter bursts into flame when thrust into a jar of nitrous oxid. Feebly burning sulfur has too low a temperature to decompose nitrous oxid and is extinguished. Vigorously burning sulfur, however, decomposes the gas and then burns very readily.
- (d) Uses.—Nitrous oxid is an anesthetic and finds extensive use in minor surgical operations. Mixed with air and inhaled it produces a kind of hysterical intoxication. Hence it is commonly called "laughing gas."
- 169. Nitric Oxid.—(a) Preparation.—When we studied the action of nitric acid on metals we learned that nitric oxid is produced by the action of moderately concentrated nitric acid on copper (see equation under (4), paragraph 164).

- (b) Physical Properties.—Nitric oxid is a colorless gas, slightly heavier than air and very slightly soluble in water.
- (c) Chemical Properties.—The most important chemical property of nitric oxid is its ability to unite with more oxygen when exposed to the air or oxygen (Fig. 59). The following reaction is reversible:

 $2NO + O_2 \rightleftharpoons 2NO_2$ .



Fig. 59.—The colorless nitric oxid unites with oxygen to form the reddishbrown nitrogen peroxid.

Nitric oxid is quite stable. It does not support ordinary combustion. Vigorously burning phosphorus decomposes it and continues to burn, uniting with the oxygen which is liberated.

Nitric oxid combines with certain salts such as ferrous sulfate. This reaction serves as a delicate test for nitric acid or nitrates. When ferrous sulfate is mixed with a nitrate and sulfuric acid poured down the side of the tube containing the mixture, the nitric acid set free by the sulfuric acid is reduced by the ferrous sulfate forming nitric oxid. The nitric oxid combines with the excess ferrous

sulfate to form a reddish-brown to black ring at the surface of the sulfuric acid layer.

- (d) Uses.—The ease with which nitric oxid combines with oxygen at the ordinary temperature and gives it up again when heated makes it a valuable carrier of oxygen. In one process of making sulfuric acid it is used to oxidize sulfur dioxid to the trioxid, which is an anhydrid of sulfuric acid.
- 170. Nitrogen Peroxid.—In the preceding paragraph we learned that nitrogen peroxid is formed when nitric oxid is exposed to the air. It may be formed by heating nitrates, sodium, potassium, and ammonium nitrates excepted.

At ordinary temperatures it is a reddish-brown gas, having a disagreeable suffocating odor. Its molecular weight shows that its formula is NO<sub>2</sub>. At low temperatures the color practically disappears and the molecular weight increases, showing that it has the formula N<sub>2</sub>O<sub>4</sub>. Such association of molecules at low temperatures and dissociation at higher temperatures is not uncommon in chemistry. The reversible equation follows:

# $2NO_2 \rightleftharpoons N_2O_4$ .

Nitrogen peroxid is unstable enough to support ordinary combustion very readily. It is very soluble in water, nitric acid being formed by such solution.

Nitrogen peroxid is a very useful oxidizing agent.

### SUMMARY

Nitric acid is prepared by heating a mixture of sodium nitrate and sulfuric acid.

Nitric acid is a heavy, oily, colorless liquid; it boils at 86°C. In water solution the acid is fairly stable. In very dilute solution it may act as an acid. In concentrated solution it is a vigorous oxidizing agent. Nitric acid seldom liberates hydrogen when it acts on metals; it usually

liberates nitric oxid or nitrogen peroxid and forms nitrates of the metal.

Nitric acid finds extensive use in the preparation of nitrates, in the dye industry, and in the manufacture of explosives.

Nitrogen forms a series of five oxids. Nitrous oxid is used as an anesthetic; nitric oxid is a carrier of oxygen; nitrogen trioxid, nitrogen peroxid, and nitrogen pentoxid are valuable oxidizing agents.

## QUESTIONS AND PROBLEMS

- 1. Why does nitric acid acquire a yellow color when exposed to sunlight?
- 2. Why would modern warfare be practically impossible without nitric acid?
- 3. State as many arguments as you can in favor of an appropriation by Congress to be used in operating a huge plant to manufacture nitric acid from air.
- 4. What per cent. of nitric oxid, NO, is oxygen? What per cent. of nitrous oxid is oxygen? Since the former has the higher per cent. of oxygen, why is the latter a better supporter of combustion?
- 5. A sample of sodium nitrate is 90 per cent. pure. How many pounds of nitric acid can be made from 1 ton of the nitrate?
- 6. A sample of potassium nitrate is 90 per cent. pure. How many pounds of nitric acid can be made from 1 ton of this nitrate? Potassium nitrate costs more per pound than sodium nitrate. If they were the same price per pound which would you use to prepare nitric acid?
- 7. Why is it impossible to remove nitric acid stains from clothing?
- 8. Given a jar of oxygen and one of nitrous oxid. By what properties would you distinguish them?
- 9. Nitric acid was formerly called aqua fortis. Can you see a good reason for such a name?
- 10. Why can not nitric acid be used for the preparation of hydrogen?

## CHAPTER XIX

## SULFUR AND HYDROGEN SULFID

171. Occurrence.—Sulfur is very widely distributed, occurring both native, or uncombined, and in such compounds as sulfids and sulfates. Free sulfur is especially

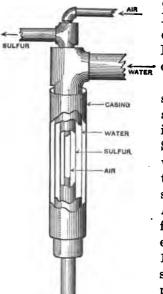


Fig. 60.—Frasch process.

common in volcanic regions.

Formerly the bulk of the sulfur came from Sicily, but at present Louisiana is producing large quantities.

172. Frasch Process.—The sulfur beds in Louisiana lying at a depth of about 500 ft. are in some places 200 ft. thick. Since these beds are covered with quick-sand, several tempts to mine the sulfur resulted in failure. Frasch, an American chemist, devised the following successful method of extracting the element. 12-in, shaft is drilled to sulfur beds and cased with iron Inside this casing three concentric pipes, 6 in., 3 in., and 1 in. in diameter respec-

tively, are driven, extending down into the sulfur beds (Fig. 60). Into the outer pipe superheated water at a pressure of 100 lbs. is forced. Its temperature is high

enough to melt the sulfur. Hot compressed air which is forced down the inner pipe mixes with the molten sulfur and decreases its specific weight so much that it is easily raised to the surface through the middle pipe (see Fig. 61). The molten sulfur is run into wooden bins 20 ft. wide and in some cases 100 ft. long and 30 to 50 ft. high. When the sulfur solidifies the sides of the box are removed,



Fig. 61.—Stream of molten sulfur issuing from a sulfur well.

the huge block which may weigh as much as 160,000 tons is blasted and loaded on cars with steam shovels (Fig. 62).

173. Purification of Sulfur.—The Louisiana sulfur is so pure (99 per cent.) that for most purposes it does not require further treatment. Crude sulfur may be purified, however, by distilling it in earthenware retorts. The vapor condenses on the walls and floor of a large brick chamber. The fine powder is called *flowers of sulfur*. The sulfur that condenses on the floor of the chamber usually melts and is

drawn off into molds to solidify. This product is called roll sulfur, or brimstone.

174. Physical Properties of Sulfur.—Ordinary sulfur is a yellow crystalline solid. It is practically insoluble in water but it dissolves quite readily in carbon disulfid and in the soluble bases. When acids are added to its solution in a base the sulfur is precipitated as a fine white powder called



Fig. 62.—A block of Louisiana sulfur. (160,000 tons.)

lac sulfur, or milk of sulfur. Ordinary sulfur melts at 114.5°C. forming a pale yellow, mobile liquid. When it is heated still higher, instead of becoming still more mobile as liquids usually do, its viscosity increases. At a temperature of about 250°C. it becomes so thick that it hardly flows from an inverted tube. The color also changes, becoming almost black. When heated still higher, sulfur again becomes more fluid; it boils at 445°C. The physical properties of sulfur are rather difficult to discuss, since

solid sulfur exists in three different allotropic forms, each having distinct properties.

(a) Rhombic Sulfur.—Rhombic sulfur is produced when sulfur crystallizes from solution. Roll sulfur dissolves in carbon disulfid readily. As the solution evaporates

the sulfur crystallizes in nearly perfect octahedra (see Fig. 63). Rhombic sulfur is stable at the ordinary temperature; its specific weight is a little more than 2.

(b) Prismatic Sulfur.—Prismatic sulfur is formed when sulfur crystallizes from the molten state. If we melt sulfur in a large crucible, cool





Fig. 63.—Rhombic sulfur crystals.

it slowly until a crust forms, break the crust and pour off the excess liquid, the interior will contain a mass of pointed needle-like crystals. They belong to the *monoclinic* system of crystallization (see Fig. 64). Monoclinic or prismatic sulfur is soluble in carbon disulfid; its specific weight is a



Fig. 64.—Needle-like crystals of prismatic sulfur.

little less than 2. At temperatures below 96°C. it gradually changes into the rhombic form.

(c) Amorphous Sulfur.—Non-crystalline sulfur is formed when boiling sulfur is cooled by pouring it into cold water. It is plastic and elastic. Its color is a dark brown.

Amorphous sulfur does not dissolve in any ordinary solvent; at the ordinary temperature it changes slowly into the rhombic modification. Thus we see that the stability of the different allotropic forms of sulfur depends upon the temperature (Fig. 65).

175. Chemical Properties.—At the ordinary temperature sulfur is quite inactive. At higher temperatures it is quite

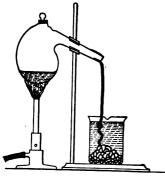


Fig. 65.—Amorphous sulfur.

as active as oxygen. It unites with oxygen forming sulfur dioxid.

$$S + O_2 \rightarrow SO_2$$
.

It combines with hydrogen forming hydrogen sulfid, H<sub>2</sub>S. When metals are heated with sulfur the union of the two elements is so energetic that heat and light are evolved. The product formed is a

sulfid. Compounds of sulfur and the non-metals are not formed so readily, and they are quite unstable. Chemically sulfur behaves in a manner analogous to oxygen. The following list of compounds shows the similarity between sulfur and oxygen compounds. If the oxid of a metal is insoluble, the sulfid is generally insoluble.

Hydrogen sulfidH <sub>2</sub> S	$Hydrogen oxidH_2O$
Copper sulfidCuS	Copper oxidCuO
Zinc sulfidZnS	Zinc oxidZnO
Magnesium sulfidMgS	Magnesium oxidMgO

176. Uses of Sulfur.—Sulfur is used in making sulfur dioxid, carbon disulfid, sulfites, thiosulfates, and to some extent in the manufacture of sulfuric acid. At one time sulfur was extensively used for making matches, fireworks,

and black gunpowder, but its use for these purposes is now somewhat limited. Considerable sulfur is now used in preparing sulfur colors.

When sulfur is mixed with rubber and heated moderately for several hours *vulcanized* rubber is formed. The product is elastic and impervious. Its hardness depends upon the relative amount of sulfur used and the heat applied. *Ebonite* is a black variety of hard rubber.

Sulfur is boiled with lime and water to prepare *lime* sulfur spray which finds extensive use in killing insects and fungi that damage fruit trees.

## HYDROGEN SULFID

177. Preparation.—Although hydrogen combines directly with molten sulfur to form hydrogen sulfid yet this method, of preparing the gas is not practical since the action is reversible.

Hydrogen sulfid is generally prepared by the action of an acid on the sulfid of a metal. Iron sulfid and hydrochloric acid interact as represented by the following equation:

$$\uparrow FeS + 2HCl \rightarrow FeCl_2 + H_2S.$$

- 178. Physical Properties.—Hydrogen sulfid is a colorless gas; it has a disagreeable odor resembling rotten eggs. It is heavier than air and moderately soluble in water. The gas is poisonous when inhaled, small quantities producing nausea, headache, and dizziness.
- 179. Properties, Chemical.—The chemical properties of hydrogen sulfid are quite important; they may be grouped as follows:
  - 1. Hydrogen Sulfid Burns.—When the supply of air or oxygen is sufficient for complete oxidation, the hydrogen is oxidized to water and the sulfur to sulfur dioxid.

$$\uparrow$$
 2H<sub>2</sub>S + 3O<sub>2</sub>  $\rightarrow$  2SO<sub>2</sub> + 2H<sub>2</sub>O.

In an insufficient supply of air hydrogen sulfid burns forming water and free sulfur.

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$
.

It is also possible to have just enough oxygen to form a mixture of water, sulfur dioxid, and sulfur. When a solution of hydrogen sulfid is exposed to the air slow oxidation occurs, sulfur being precipitated.

2. Hydrogen Sulfid a Reducing Agent.—Since hydrogen's sulfid decomposes easily into hydrogen and sulfur, it is a good reducing agent, for sulfur and hydrogen both have a strong affinity for oxygen. If the gas is passed through a solution of hydrogen peroxid, it reduces the peroxid to water. At the same time the hydrogen of the gas is oxidized. Sulfur is precipitated in the form of a fine white powder.

$$H_2O_2 + H_2S \rightarrow 2H_2O + S.$$

- 3. Hydrogen Sulfid an Acid.—In water solution the gas turns blue litmus red, neutralizes bases, and behaves in other ways like a weak acid. Its water solution is often called hydrosulfuric acid.
- 4. Hydrogen Sulfid Acts on Metals.—The water solution of hydrogen sulfid acts on metals forming sulfids. Organic substances, especially eggs, mustard, etc., contain considerable sulfur. As they decay hydrogen sulfid is formed. A silver spoon left in contact with such foods soon becomes covered with a coating of silver sulfid. The tarnishing of some other metals is due to the formation of a sulfid.
- 180. Uses.—The most important use of hydrogen sulfid is as a reagent in qualitative analysis. Nearly all metallic sulfids are insoluble in water. If we add hydrogen sulfid to solutions of the salts of several metals the insoluble sulfids of these metals will be thrown down as precipitates.

$$\begin{array}{c} \operatorname{Cu(NO_3)_2} + \operatorname{H_2S} \to \operatorname{CuS} + 2\operatorname{HNO_3}. \\ \downarrow \\ 2\operatorname{AsCl_3} + 3\operatorname{H_2S} \to \operatorname{As_2S_3} + 6\operatorname{HCl}. \\ \downarrow \\ \operatorname{SnCl_4} + 2\operatorname{H_2S} \to \operatorname{SnS_2} + 4\operatorname{HCl}. \\ \downarrow \\ \downarrow \end{array}$$

The mixture of sulfids may be separated from one another since their solubility in other reagents varies. For example, zinc sulfid and manganese sulfid are soluble in dilute hydrochloric acid; arsenic sulfid and tin sulfid are soluble in ammonium sulfid; the sulfids of copper and lead are soluble in hot nitric acid while mercuric sulfid is insoluble. A scheme for the separation of the compounds of metals in solution has been worked out, based to some extent upon the solubilities of their sulfids in certain reagents.

- 181. Sulfur Springs.—Hydrogen sulfid is found in certain natural springs and in artesian waters. It imparts a disagreeable odor to the water and a peculiar taste. As oxidation occurs when the water comes into contact with the air the sulfur is deposited. Some sulfur springs are supposed to have certain medicinal properties.
- 182. Carbon Disulfid.—Carbon disulfid, CS<sub>2</sub>, is a compound prepared by the action of sulfur vapor on charcoal in an electric furnace. It is a heavy oily liquid; nearly colorless. The commercial product has a very disagreeable odor. It is not miscible with water. Its vapor is very inflammable, the products of combustion being sulfur dioxid and carbon dioxid.

It is used as a solvent for sulfur, phosphorus, waxes, and resins. A solution of rubber in carbon disulfid is used as rubber cement. Carbon disulfid is used quite extensively for destroying insects and other small animals, since its vapor is poisonous and the products of its combustion are suffocating.

#### SUMMARY

Sulfur occurs in volcanic regions. It is believed that beds of sulfur are sometimes formed by the decomposition of sulfates in the presence of bacteria.

Crude sulfur is purified by distillation. It is sold as flowers of sulfur, roll sulfur, and lac sulfur.

Sulfur exists in three solid allotropic forms; rhombic sulfur, prismatic sulfur, and amorphous sulfur. Sulfur is about twice as heavy as water; it is insoluble in water but dissolves readily in carbon disulfid.

Sulfur burns with a pale blue flame forming sulfur dioxid. It unites readily at higher temperatures with most metals.

Hydrogen sulfid is prepared by the action of an acid on a sulfid. It is a colorless gas with a very disagreeable odor. The gas is heavier than air and soluble in water.

Hydrogen sulfid burns with a blue flame. It is a reducing agent. In water solution it acts like an acid and it combines with metals to form sulfids. It is used in qualitative analysis.

Carbon disulfid is an oily liquid; it burns readily. It is used as a solvent, and as a germicide and insecticide.

# QUESTIONS AND PROBLEMS

- 1. Write three equations for the burning of hydrogen sulfid, varying the amount of oxygen used.
- 2. How many liters of oxygen would be required in each of the above equations to combine with 8 liters of hydrogen sulfid?
- 3. Would nitric acid be suitable for use in preparing hydrogen sulfid? Explain.
  - 4. Devise a method of testing for traces of hydrogen sulfid.
  - 5. Calculate the weight of 1 liter of hydrogen sulfid.
- 6. How many grams of iron sulfid are needed to prepare 30 grams of hydrogen sulfid? To prepare 20 liters of the gas?
  - 7. Why does silverware tarnish so readily in city dwellings?
- 8. Write the equations to show the reaction of hydrogen sulfid on the chlorids of mercury, antimony, zinc, nickel, and bismuth.

### CHAPTER XX

## OXIDS AND ACIDS OF SULFUR

- 183. Preparation of Sulfur Dioxid.—1. Burning Sulfur.—When sulfur burns in air, sulfur dioxid, SO<sub>2</sub>, is formed. Since the product mixes with nitrogen and other atmospheric constituents, this method is not practical if reasonably pure sulfur dioxid is desired. Metallic sulfids yield sulfur dioxid when heated or roasted in air.
- 2. Reduction of Sulfuric Acid.—Hot concentrated sulfuric acid acts as an oxidizing agent in the presence of certain metals. A part of the sulfuric acid is thus decomposed with the liberation of sulfur dioxid. The reaction is complex but probably a series of reactions occurs about as follows:

$$\begin{array}{c} H_2SO_4 \rightarrow H_2O + SO_2 + (O) \\ \\ Cu + O \rightarrow CuO \\ \hline \\ CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \end{array}$$

If we combine these equations, the final products may be represented as follows:

$$\begin{array}{c}
 \uparrow \\
 \text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2.
 \end{array}$$

3. Decomposition of Sulfites.—Sulfur dioxid is frequently prepared by the action of an acid on a sulfite. If sodium sulfite and sulfuric acid are used the products formed are water, sulfur dioxid, and sodium sulfate.

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2SO_3$$
  
 $SO_2 + H_2O.$ 

- 184. Properties, Physical.—Sulfur dioxid is a colorless gas with a choking odor. As prepared in the laboratory it is usually whitish in appearance due to the presence of finely divided particles of sulfur trioxid. Sulfur dioxid is more than twice as heavy as air; it is very soluble in water. It is one of the easiest gases to liquefy, and liquid sulfur dioxid is put on the market in metal containers.
- 185. Properties, Chemical.—1. Activity.—Sulfur dioxid neither burns nor supports combustion, although it may be oxidized to sulfur trioxid by using suitable catalytic agents. Thus it acts chemically as a reducing agent.
- 2. Acid Action of Sulfur Dioxid Solution.—Sulfur dioxid is the anhydrid of sulfurous acid. When sulfur dioxid is dissolved in water the solution has the properties of a weak acid, turning blue litmus red, and neutralizing bases forming sulfites. Sulfurous acid is unstable readily breaking up into water and sulfur dioxid.

$$H_2SO_3 \rightarrow H_2O + SO_2$$
.

- 3. Bleaching Action.—Sulfur dioxid unites with the colored compounds of many organic substances forming colorless compounds. For example, sulfur dioxid unites with the natural yellow color of straw to form a colorless compound. The substance to be bleached must be moist. It is possible that the bleaching action of sulfur dioxid is sometimes due to its ability to act as a reducing agent.
- 186. Uses of Sulfur Dioxid.—Sulfur dioxid is used as a disinfectant and insecticide. It prevents the growth of yeasts, molds, and bacteria. Hence it is sometimes used as a preservative in such food-stuffs as canned corn, sausage, and fruits. Since it is injurious to higher forms of life as well as to lower animal and plant life, its use as a preservative is questionable.

Considerable sulfur dioxid is used to bleach wool, silk, and straw. The colorless compound that is formed by the union of the dioxid with the natural color is unstable; it decomposes in sunlight giving the original color. Certain food-products, such as molasses and dried fruits are often bleached by sulfur dioxid. Maraschino cherries are thus bleached and then dyed a bright red or green color (see Fig. 66).

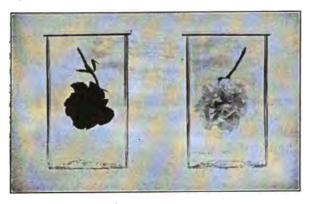


Fig. 66.—Carnations showing the bleaching effects of sulfur dioxid.

Large quantities of sulfur dioxid are used in the preparation of sulfites but its most important use is in the manufacture of sulfuric acid.

#### SULFUR TRIOXID AND SULFURIC ACID

187. Sulfur Trioxid.—Sulfur trioxid is the anhydrid of sulfuric acid. It is a colorless liquid at ordinary temperature. In the presence of a trace of moisture it forms a white crystalline solid. This solid dissolves in water with a hissing sound forming sulfuric acid. Sulfuric anhydrid is a vigorous oxidizing agent.

188. Manufacture of Sulfuric Acid.—We have learned that sulfuric acid is formed by dissolving its anhydrid, SO<sub>2</sub>, in water.

$$H_2O + SO_3 \rightleftharpoons H_2SO_4$$
.

In making the acid commercially two processes are in extensive use.

1. Contact Process.—When sulfur dioxid is heated with air sulfur trioxid is formed slowly. In the presence of a suitable catalytic agent, such as ferric oxid or finely divided platinum, the union of the oxygen with the sulfur dioxid,  $2SO_2 + O_2 \rightarrow 2SO_3$ , occurs rapidly enough so that the method may be used commercially.

The sulfur dioxid, obtained by roasting iron pyrites, FeS<sub>2</sub>, is mixed with air and passed through heated iron pipes containing the catalyzer. The sulfur trioxid that is formed is usually absorbed in very concentrated sulfuric acid and then diluted with water to the desired strength.

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7.$$
  
 $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4.$ 

The contact process of making sulfuric acid is used extensively in Europe, especially when chemically pure acid of a high concentration is required.

2. Chamber Process.—In the chamber process sulfur dioxid is oxidized to the trioxid by the use of oxids of nitrogen; the sulfur trioxid combines with water to form sulfuric acid. We have seen that nitric oxid acts as a carrier of oxygen, taking it from the air and giving it up to a reducing agent such as sulfur dioxid; thus the oxids of nitrogen are not wasted but used again and again (see Fig. 67).

In practice the sulfur dioxid, formed by burning sulfur or roasting iron pyrites,  $FeS_2$ , together with oxids of nitrogen and an excess of air, is conducted from the burners B into the Glover tower. As the gases ascend through the tower, which is filled

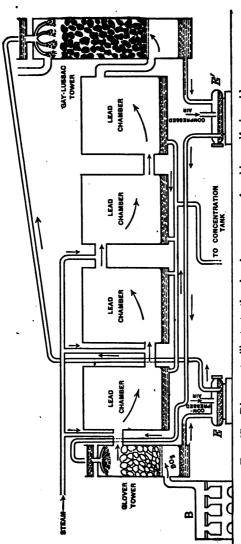


Fig. 67.—Diagram to illustrate the chamber process of making sulfuric acid.

with lumps of quartz, or some acid-resisting brick, they meet two streams of sulfuric acid, one dilute and the other containing dissolved oxids of nitrogen, from the Gay-Lussac tower. These acids cool the ascending gases before they enter the lead chambers. The acid from the Gay-Lussac tower loses its oxids of nitrogen and the dilute acid loses water, so that a more concentrated acid flows from the bottom of the tower into the acid egg E from which it is forced by compressed air to the top of the Gay-Lussac tower.

The main chemical reactions occur in the lead chambers, which may be 100 ft. long, 40 ft. high, and 20 ft. wide. Four of these chambers are generally used in a single plant. Steam is introduced, which combines with the gases entering the chambers from the top of the Glover tower to form the chamber acid. Sulfuric acid does not act on lead until it is fairly concentrated, nearly 80 per cent. For many industrial purposes the acid does not need further concentration. If a more concentrated acid is desired, further concentration is carried on in glass or platinum vessels. As the concentration of this acid is the most costly part of the process, the bulk of the concentrated acid of commerce is now made by the contact process.

Some of the oxids of nitrogen from the last chamber are absorbed in the Gay-Lussac tower by concentrated acid from the Glover tower which trickles down over layers of coke. This "nitrose" acid flows into the egg E' from which it is forced to the top of the Glover tower to be used over again. Waste gases, including nitrogen and some of the lower oxids of nitrogen, pass out through a stack at the top of the Gay-Lussac tower.

189. Physical Properties.—Sulfuric acid is a heavy, oily liquid; it is frequently called "oil of vitriol." Ordinary concentrated sulfuric contains about 93.5 per cent. acid; its specific weight is from 1.83 to 1.84. The boiling point of this acid is higher than that of most common acids, about 338°C. Pure sulfuric acid is colorless but the commercial acid is often colored yellow to almost black due to impurities, especially organic matter. When sulfuric acid is added to water, a great deal of heat is evolved. The action is chemical, hydrates of sulfuric acid, H<sub>2</sub>SO<sub>4</sub>.

- 190. Chemical Properties.—1. As an Acid.—Dilute sulfuric acid has all the properties of a typical acid. It acts on metals, the oxids of metals, and neutralizes bases forming sulfates.
- 2. As an Oxidizing Agent.—When heated, sulfuric acid decomposes as follows:  $H_2SO_4 \rightarrow H_2O + SO_2 + (O)$ . The nascent oxygen is a vigorous oxidizing agent. Thus hot concentrated sulfuric acid acts as an oxidizing agent exactly analogous to hot nitric acid, although it is not so vigorous in its action. Its action on metals when hot and concentrated was shown in the second method of preparing sulfur dioxid. The dilute acid acts on metals liberating hydrogen.
- 3. As a Dehydrating Agent.—Sulfuric acid has a strong affinity for water. Gases that do not interact with the acid may be dried by bubbling them through it. In making explosives the action of nitric acid on the organic matter forms water. Sulfuric acid is always mixed with the nitric acid to absorb the water that is thus formed and prevent its dilution. Not only does sulfuric acid absorb water, but it takes hydrogen and oxygen from many organic compounds leaving carbon as a residue. In this manner sulfuric acid chars wood, paper, cotton, and other organic matter. Continued action of the hot acid may completely oxidize the carbon.
- 191. Uses.—To mention all the uses of sulfuric acid would necessitate naming nearly all the industries. Enormous quantities of sulfuric acid are used in the petroleum industry, in making explosives, fertilizers, and in the preparation of nearly all other acids. The commercial acid can be manufactured for less than a cent a pound.
- 192. Sulfates.—The sulfates form a very important class of salts. They are salts of sulfuric acid; they are often popularly called vitriols. Copper sulfate is commonly

called blue vitriol; zinc sulfate, white vitriol; and ferrous sulfate, green vitriol. All sulfates have the SO<sub>4</sub> radical. Nearly all sulfates are soluble, the sulfates of lead, calcium, strontium, and barium being the chief exceptions.

- 193. Test for a Sulfate.—When a solution of barium chlorid is added to a solution containing sulfuric acid, or a sulfate, a white precipitate of barium sulfate is formed. This precipitate is insoluble in hydrochloric acid. The above test is used to detect the presence of a sulfate.
- 194. Normal Salts and Acid Salts.—Sulfuric acid has 2 hydrogen atoms per molecule, one or both of which may be replaced by the metal of a base. An acid having 2 replaceable hydrogen atoms per molecule is said to be dibasic. It can form two classes of salts: normal or neutral, and acid. The following equations show how this is possible.

The dotted lines show that each hydrogen atom of the sulfuric acid molecule unites with one hydroxyl (OH) group to form a molecule of water. Sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>, is a *normal* salt.

If we use just half as much sodium hydroxid the reaction takes place as follows:

Only one of the hydrogen atoms of the sulfuric acid molecule unites with hydroxyl to form water and the salt formed is acid sodium sulfate, HNaSO<sub>4</sub>; since the salt has

nearly twice as much (SO<sub>4</sub>) for a given weight of sodium as sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>, it is often called sodium bi-sulfate.

A glance at the formulas of nitric acid and hydrochloric acid shows that they can form normal salts only, since they have only 1 hydrogen atom to the molecule. Such acids are mono-basic.

Phosphoric acid, H<sub>8</sub>PO<sub>4</sub>, is a *tri-basic acid*; it has 3 replaceable hydrogen atoms in its molecule. It may form three classes of salts as the following equations clearly show.

Na<sub>3</sub>PO<sub>4</sub> is tri-sodium phosphate, or normal sodium phosphate.

HNa<sub>2</sub>PO<sub>4</sub> is di-sodium phosphate, or acid sodium phosphate. H<sub>2</sub>NaPO<sub>4</sub> is mono-sodium phosphate, or di-acid sodium phosphate.

195. Other Acids of Sulfur.—A large number of acids of sulfur are known. With the exception of those already discussed, few are very important. Hypo-sulfurous acid probably has the formula H<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. Per-sulfuric acid,

 $H_2S_2O_8$ , is a very vigorous oxidizing agent. Pyro-sulfuric acid, or fuming sulfuric acid is  $H_2S_2O_7$ . Thio-sulfuric acid,  $H_2S_2O_3$ , is unstable but its sodium salt forms the "hypo" used so extensively by photographers.

#### SUMMARY

Sulfur dioxid is formed: (1) by burning sulfur; (2) by roasting sulfids; (3) by decomposing sulfuric acid; and (4) by the action of an acid on a sulfite.

Sulfur dioxid is a heavy suffocating gas; it is very soluble in water; sulfur dioxid is very easy to liquefy.

Chemically sulfur dioxid is a reducing agent; its water solution has all the properties of a weak acid. Sulfur dioxid is a good disinfectant and antiseptic.

Sulfur dioxid is used as a germicide, a preservative, a bleaching agent, and in the preparation of sulfites and sulfuric acid.

Sulfur trioxid is prepared by oxidizing sulfur dioxid by the use of a suitable catalytic agent. Sulfur trioxid is the anhydrid of sulfuric acid.

Sulfuric acid may be made by the contact process or the chamber process. It is a heavy oily liquid that mixes with water in all proportions. Chemically sulfuric acid acts as an acid when dilute; it acts as an oxidizing agent when concentrated and also as a dehydrating agent.

Sulfuric acid is used in nearly all industries.

A di-basic acid has 2 replaceable hydrogen atoms per molecule; it forms two classes of salts: acid salts, and normal salts.

# QUESTIONS AND PROBLEMS

- 1. State two reasons why sulfuric acid is used in the preparation of other acids.
  - 2. How would you prepare pure sulfur dioxid?
- 3. In diluting sulfuric acid why should the sulfuric acid be poured into the water?

- 4. How many pounds of sulfuric acid can be prepared from 1 ton of sulfur, if its purity is 98 per cent.?
- 5. Would it be possible for sulfuric acid to form an acid salt with calcium hydroxid? If so, write the equation.
- 6. Cream of tartar is a salt. How do you account for its sour taste and its action as an acid?
- 7. How many sodium salts could be formed with a tetra-basic acid?
- 8. How would you test a solution to see whether it contains a sulfate?
- 9. How many cubic centimeters of sulfuric acid, specific weight 1.8, strength 87 per cent., will be required to neutralize 100 grams of sodium hydroxid?

Topics for Reference.—Sulfur dioxid as a bleaching agent.

## CHAPTER XXI

#### THEORY OF SOLUTION—IONIZATION

196. Introductory.—It has long been known that certain substances behave very differently in solution than they do in the dry state. (1) They are more active chemically; in fact in the majority of cases it is doubtful if any chemical action occurs between perfectly dry substances. (2) Certain dry substances are poor conductors of electricity, while their water solution conducts the electric current fairly well. (3) Substances whose solutions are fair conductors of electricity produce abnormal osmotic pressure. (4) Such substances also lower the freezing point and raise the boiling point of their solutions abnormally.

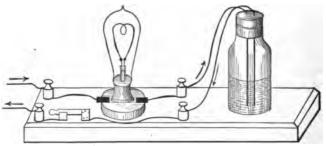


Fig. 68.—Apparatus used to show the conductivity of solutions.

197. Electrolytes and Non-electrolytes.—Chemical compounds whose water solutions are good conductors of electricity are called *electrolytes*. By using the apparatus shown in Fig. 68, we may test the conductivity of certain substances. If we add a little hydrochloric acid to the



(Permission of Popular Science Monthly.)

Charles Martin Hall (1863-1914) was an American inventor. While student at Oberlin College he became interested in aluminum and began his research work in an effort to extract the metal at a lower cost. The reduction of aluminum oxid is difficult and the ore is not easily fused. Hall discovered that it dissolves readily in cryolite, a compound that is readily fusible. From such a solution aluminum may be obtained by electrolysis. Hall was awarded the Perkin medal in 1911.

Svante Arrhenius (1859-—) is a Swedish physical In 1891 he was chemist. made Professor of Chemistry at the University of Stockholm. In 1887 he proposed the modern theory of the dissociation of electrolytes in solution. His ionization theory has done much to explain many observations over which chemists had long puzzled. He was awarded the Nobel prize in 1903.



(Permission of Current Opinion.)



bottle and dip the wires into the solution the electric light glows brightly. Other acids behave in the same manner, although in most cases the light does not glow so brightly showing that most acids do not conduct the current so readily as hydrochloric acid. In the same manner we may test the soluble bases and salts. They are also conductors. Thus we conclude that acids, bases, and salts are electrolytes. Distilled water does not conduct the current and the lamp does not glow when the wires are dipped into it. The addition of such substances as alcohol, ether, sugar, glycerin, and glucose does not render the solution conducting. Such substances are non-electrolytes.

198. Ionization Theory.—Of several theories of solution that have been advanced, the one that seems most plausible was proposed by Arrhenius, a Swedish chemist, in 1887. His theory of *ionization* is probably more generally accepted at the present time than any other theory of solution.

This theory of solution assumes that electrolytes in solution are dissociated into ions. An ion is an atom or group of atoms that carries an electric charge. To illustrate, suppose we dissolve sodium chlorid in water. Part of the sodium chlorid molecules dissociate into sodium ions and chlorid ions. The sodium ion carries a positive charge; the chlorid ion, a negative charge. The following ionic equation shows the manner of dissociation

$$+$$
 - NaCl + H<sub>2</sub>O  $\rightarrow$  Na Cl + HOH.

Some of the sodium chlorid molecules are not dissociated, but the percentage that dissociates increases as the solution becomes more dilute. Concentrating a solution by evaporating the water decreases the number of ions present, the solid salt being again obtained by evaporating to dryness. Water itself is *very* slightly ionized, forming positive hydrogen ions and negative hydroxyl (OH) ions.

199. Ion and Atom.—The opponents of the ionization theory state that if dissociation occurs in solution, as in the case of sodium chlorid, the sodium would attack the water forming sodium hydroxid and that the chlorin would color the solution yellow. It appears that the electric charge carried by the atom changes its nature. As soon as the sodium ion gives up its positive charge it behaves in every way like a sodium atom. The same is true of the chlorin ion. Since there are the same number of positive charges as negative the solution shows no signs of being electrically charged.

200. Electrolysis.—The ionization theory explains why some solutions conduct the electric current. In Fig. 69,

suppose we have a solution of copper sulfate. As the salt dissolves, dissociation occurs.



Fig. 69.—Dissociation of copper sulfate into its ions.

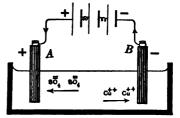


Fig. 70.—Electrolysis of copper sulfate.

Since copper is bivalent, each copper ion carries two positive charges; each sulfion (SO<sub>4</sub>) group carries two negative charges.

Suppose we introduce into the solution two platinum strips, or carbon rods, and connect them to a battery as in Fig. 70. Since the rod A is connected to the positive plate of the battery it is charged positively; it is called the positive electrode, or anode. The rod B which is connected to the negative plate becomes negatively charged; it is called the negative electrode, or cathode. Since like charges repel each other and unlike charges attract, the copper ions will go to the cathode. There they have their charge

neutralized, and are deposited on the cathode as a smooth coating of metallic copper. The SO<sub>4</sub> ions are attracted to the anode; as their charge is neutralized the SO<sub>4</sub> group, being unstable, breaks up liberating oxygen and forming SO<sub>3</sub>. The SO<sub>3</sub> unites with water to form sulfuric acid.

Electrolysis is the separation of a compound into its constituents by means of an electric current. The student should remember that dissociation occurs before the electrodes are introduced; the electric current separates the ions, the positive going to the cathode and the negative to the anode. The ions really conduct the current through the solution.

201. Effect of Electrolytes on the Boiling Point and Freezing Point.—We have already learned that 1 mole of certain substances dissolved in 1 liter of water lowers the freezing point 1.89°C. and raises the boiling point 0.52°C. Following a series of investigations Van't Hoff formulated the following theory: Dilute solutions of equal osmotic pressure contain the same number of molecules. His theory is really Avogadro's theory applied to dilute solutions. It appears then that the effect a solute has on the boiling point and freezing point is due to the number of particles in solution.

The fact that a molar solution of sodium chlorid lowers the freezing point nearly twice as much as a molar solution of sugar is easily explained by the ionic theory. As the sodium chlorid ionizes each molecule forms two ions or particles. Hence in dilute solutions when the ionization is nearly complete there will be nearly twice as many particles as in a solution of a non-electrolyte of equal concentration. The boiling point will also be raised nearly twice as much.

202. Degree of Ionization.—From the preceding paragraph it is easy to determine the degree of ionization of a substance in solution. If the electrolyte were completely ionized, the freezing point of the solution would be lowered

twice as much as with a non-electrolyte of the same concentration. Suppose a solution of sodium chlorid when tested lowers the freezing point only 1.8 times as much as a non-electrolyte. It is evident that only 1.8/2, or 90 per cent. of the sodium chlorid molecules are ionized. The degree of ionization can be more accurately determined by measuring the conductivity of the solution, but the method is too difficult for beginners.

203. Ionization of Acids.—All acids contain hydrogen. When they ionize the hydrogen ion is positive. Hydrochloric acid ionizes as follows: H Cl; nitric acid, H NO<sub>8</sub>. An acid may be defined as a compound whose water solution contains positive hydrogen ions.

From the above definition the strength of an acid appears to depend upon the number of hydrogen ions present in its solution. Since hydrochloric acid and nitric acid ionize readily they form some of the strongest acids known. The student must not confuse the terms strong and concentrated as applied to acids. Dilute hydrochloric acid contains more hydrogen ions than concentrated acetic acid which does not ionize readily. Hence acetic acid is a weak acid. Dry hydrogen chlorid does not act as an acid at all. One hundred per cent. nitric acid is a vigorous oxidizing agent but it does not have acid properties.

Sulfuric acid undergoes two stages of ionization as follows: H HSO<sub>4</sub>; the HSO<sub>4</sub> undergoes a secondary ionization, H SO<sub>4</sub>. The ability of sulfuric acid to ionize in two separate steps accounts for the formation of normal and acid salts.

$$\stackrel{+}{\text{Na}} \stackrel{-}{\text{OH}} + \stackrel{+}{\text{H}} \stackrel{-}{\text{HSO}} \stackrel{+}{\longleftrightarrow} \stackrel{-}{\text{Na}} \stackrel{-}{\text{HSO}} \stackrel{+}{\longleftrightarrow} + \text{HOH}.$$

Sulfuric acid does not ionize so completely as hydrochloric and nitric acids and is a weaker acid, although because of its high boiling point it decomposes salts of either nitric or hydrochloric acid.

204. Ionization of Bases.—When bases ionize the metallic ion carries the positive charge and the hydroxyl (OH) ion is negative. For example, Na OH; K OH; Ca (OH)<sub>2</sub>. A base may be defined as a compound whose water solution contains negative hydroxyl (OH) ions.

The strength of a base depends upon the concentration of the (OH) ion. Sodium hydroxid and potassium hydroxid are the strongest bases known. Ammonium hydroxid of equal concentration furnishes only about 4 per cent. as many (OH) ions; it is therefore a weak base.

205. Neutralization.—When we write the ionic equation to show neutralization.

$$\stackrel{+}{N}$$
a  $\stackrel{-}{OH} + \stackrel{+}{H} \stackrel{-}{Cl} \longrightarrow \stackrel{+}{N}$ a  $\stackrel{-}{Cl} + HOH$ ,

we see that the hydrogen ion of the acid unites with the (OH) ion of the base to form non-ionized water. The salt that is formed ionizes, since soluble salts usually have a high degree of ionization. A salt may be defined as a compound formed by the union of the positive ion of the base with the negative ion of an acid.

It is interesting to note that the amount of heat liberated by neutralizing 1 mole of a mono-basic acid is the same as that liberated by the neutralization of 1 mole of any other mono-basic acid. Thus 13,700 calories of heat are liberated when 1 mole of sodium hydroxid in solution neutralizes 1 mole of hydrochloric acid; the same amount is liberated when 1 mole of the same base neutralizes 1 mole of nitric acid. This is also the heat of formation of 1 mole, or 18 grams, of water by neutralization.

206. Chemical Tests Are Tests for Ions.—In the laboratory most tests are tests for ions, not elements. If we

add to a solution of sodium chlorid a few cubic centimeters of silver nitrate solution the following reaction occurs:

$$\stackrel{+}{\operatorname{Na}}$$
  $\stackrel{-}{\operatorname{Cl}}$   $\stackrel{+}{\operatorname{Ag}}$   $\stackrel{-}{\operatorname{NO}_{s}}$   $\stackrel{+}{\operatorname{MO}_{s}}$   $\stackrel{+}{\operatorname{NO}_{s}}$   $\stackrel{+}{\operatorname{NO}_{s}}$ .

The undissociated silver chlorid comes down as a white precipitate. Insoluble silver chlorid is always precipitated when silver nitrate is added to a solution of a chlorid. That this test is not a test for *chlorin* may be shown by adding a few cubic centimeters of silver nitrate to a solution of sodium chlorate.

$$\stackrel{+}{\text{Na}}$$
  $\stackrel{-}{\text{ClO}_3}$  +  $\stackrel{+}{\text{Ag}}$   $\stackrel{-}{\text{NO}_3}$   $\rightleftharpoons$   $\stackrel{+}{\text{Ag}}$   $\stackrel{-}{\text{ClO}_3}$  +  $\stackrel{+}{\text{Na}}$   $\stackrel{-}{\text{NO}_3}$ .

Chlorin is present in sodium chlorate but no precipitate is formed with the silver nitrate. If any reaction occurs, all the substances ionize and remain in solution.

Anhydrous copper sulfate is white; the hydrated salt or a solution of the salt is blue in color. Since soluble copper salts give a blue solution we may infer that the blue color is due to the copper ion. In a similar way it may be shown that the ferrous ion is green, while the ferric ion is reddishbrown. Cobalt salts are pink in water solution when ionized, but a large number of them become blue when they are dehydrated.

The theory of ionization explains the fact that such mixtures as baking powder, effervescing powders, etc., do not act in the dry state, but that a chemical change begins as soon as water is introduced, thereby causing dissociation.

207. Valence of Ions.—From the equations that have been given showing ionization, it is easy to see that the valence of an ion is equal to the number of electrical charges the ion carries. Hydrogen is capable of losing one negative charge or electron, and thus has a positive valence of 1; aluminum has the ability to lose three electrons, hence

it has a positive valence of 3. The number of electrons a negative ion can gain, or acquire, determines its valence.

208. Ionizing Agents.—Ionization occurs very readily in water solution. It does not occur so readily in most other solvents. Hydrogen chlorid does not act like an acid when dissolved in toluol since ionization does not occur. Ionization does not occur readily in such solvents as toluol, ether, and benzol.

Heat may produce ionization. Gases that are heated to a high temperature become fair conductors of electricity since ionization takes place to some extent. Heating a solution increases the degree of ionization of the solute.

Fused or melted salts are ionized to some extent. Dry sodium chlorid is a poor conductor. The fused salt is quite a good conductor. Considerable use is made of the fact that ionization occurs when the salt is melted, especially in the electrolysis of compounds whose elements tend to unite readily with water.

#### SUMMARY

An electrolyte is a compound whose water solution is a good conductor of electricity. Acids, bases, and salts are electrolytes. Such substances as alcohol, ether, and sugar are non-electrolytes. Their solutions are non-conductors.

The ionization theory assumes that electrolytes are dissociated into ions in water solution. An ion is an atom or a group of atoms carrying an electric charge.

An acid is a compound whose water solution contains hydrogen ions; its strength depends upon the concentration of the hydrogen ion.

A base is a compound whose water solution contains hydroxyl (OH) ions; its strength depends upon the concentration of hydroxyl ions.

Neutralization is the union of the hydrogen ion of an acid with the hydroxyl ion of a base to form water.

The ionization theory explains the conductivity of solutions, the abnormal osmotic pressure of electrolytes, and the abnormal elevation of the boiling point and depression of the freezing point by electrolytes in solution.

#### QUESTIONS

- 1. Why do we call the solution of hydrogen sulfid a weak acid and the solution of hydrogen chlorid a strong acid?
- 2. What is an electrolyte? How could you determine whether glycerol is an electrolyte?
- 3. Write ionic equations to show the neutralization of nitric acid by calcium hydroxid; of sulfuric acid by calcium hydroxid.
- 4. Define acid, base, salt, and neutralization from the stand-point of the theory of ionization.
- 5. Cold, concentrated sulfuric acid does not act on zinc to liberate hydrogen, but dilute sulfuric acid does. Explain.
- 6. From a consideration of the theory of ionization explain what happens when an electric current is passed through a solution of sodium chlorid.
- 7. Substances coated with a solution of a cobalt salt show color changes depending upon the amount of moisture in the air. Explain.

Topic for Reference.—Arrhenius. Van't Hoff.

### CHAPTER XXII

# EQUILIBRIUM AND REVERSIBILITY

209. Introductory.—We know that many substances in solution are very active chemically. We have also observed that some chemical reactions run to completion, while others run to equilibrium. It will be of interest to inquire what changes occur during metathesis. If we mix solutions of silver nitrate and sodium chlorid,

$$\stackrel{+}{\operatorname{Ag}} \stackrel{-}{\operatorname{NO}_{2}} + \stackrel{+}{\operatorname{Na}} \stackrel{-}{\operatorname{Cl}} \rightarrow \operatorname{AgCl} + \stackrel{+}{\operatorname{Na}} \stackrel{-}{\operatorname{NO}_{2}},$$

we may be sure that the sodium and the silver ions will not combine since both are positive and like charges repel. Likewise we reason that the chlorid ion and the nitrate ion will not combine since both are negative. Thus the only possible combinations, if a chemical change occurs at all, will result in the union of positive silver ions with negative chlorid ions to form silver chlorid and the union of positive sodium ions with negative nitrate ions to form sodium nitrate. The student should remember that it is customary to write the positive forming element of a compound first. It is also of interest to inquire if there is any way to foretell whether a chemical reaction will occur, and whether it will run to completion or to equilibrium.

210. Chemical Reactions Run to Completion.—1. When an Insoluble Compound is Formed.—The reaction discussed in the preceding paragraph runs to completion because silver chlorid, an insoluble compound, is formed. This is what we might expect from the ionization theory. The

solutions of sodium chlorid and silver nitrate were largely ionized. The silver chlorid as it is formed does not ionize and is virtually removed from the sphere of action. As the Ag and Cl ions are thus removed other silver nitrate and sodium chlorid molecules dissociate, their Ag and Cl ions being in turn removed by the precipitation of more silver chlorid. Thus we conclude that metathesis will always occur if one of the compounds that would be formed is insoluble; such a reaction will run to completion.

2. When a Volatile Compound or Substance is Produced.—Suppose we treat sodium chlorid with sulfuric acid,

$$2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}.$$

The hydrogen chlorid that is formed is volatile and escapes as a gas. The explanation from the ionic theory is the same as above. The H and Cl ions unite to form gaseous HCl which is not dissociated. Thus we conclude that metathesis will occur if one of the compounds that would be formed is volatile; such a reaction also runs to completion. These facts are known as Berthollet's laws.

3. When a Compound is Formed That Does Not Dissociate.—Neutralization reactions usually run to completion since water, which does not ionize to any appreciable extent, is always formed,

In 10 per cent. solutions sodium hydroxid, hydrochloric acid, and sodium chlorid all dissociate to the extent of 50 per cent. or more. Water dissociates to the extent of about 1 part per billion. Thus the above reaction runs practically to completion, the H ion of the acid and the OH ion of the base uniting to form non-ionized water.

211. Equilibrium.—Suppose we mix solutions of sodium nitrate and potassium chlorid.

If metathesis occurs at all, potassium nitrate and sodium chlorid will be formed. But both these salts dissociate in solution. Thus while the sodium nitrate and potassium chlorid tend to form potassium nitrate and sodium chlorid the same products tend to reverse the reaction to form the original salts. The equation is reversible and runs to equilibrium. Such a solution will then contain Na, NO<sub>3</sub>, K, and Cl ions; it will also contain some undissociated molecules of sodium nitrate, potassium chlorid, potassium nitrate, and sodium chlorid. If we increase the concentration of one factor after equilibrium has been reached, by adding more of one of the constituents, the equilibrium is destroyed and the proportion of the constituents is varied. effect is known as mass action. It is very important to the manufacturing chemist, since changes in temperature and atmospheric pressure often influence the concentration of the ions of one substance more than another. By thus increasing the concentration on one side of the equation or decreasing it on the other, it is possible to increase the yield of a product, or to change in some cases an equilibrium reaction to one that runs to completion.

212. Hydrolysis.—Although water ionizes very slightly, yet it does dissociate to some extent. When a salt is dissolved in water, enough hydrogen and hydroxyl ions may be formed from the water to reverse the ordinary neutralization reaction by which the salt was formed. Such decomposition of a compound by water is called hydrolysis.

Sodium chlorid undergoes almost no hydrolysis in water since it is the salt of a very strong base and a very strong acid. The degree of ionization of the water is so slight in comparison with that of the acid and base that it is almost negligible.

Sodium carbonate hydrolyzes to some extent in water solution.

 $Na_2CO_3 + 2HOH \stackrel{\rightarrow}{\smile} H_2CO_3 + 2NaOH$ 

If we study this reaction we see that two of the compounds, sodium carbonate and sodium hydroxid dissociate readily; carbonic acid is a weak acid and dissociates slightly; water is very slightly dissociated. Red litmus dipped into the solution is turned blue since the small amount of sodium hydroxid formed from the OH ions of the water is relatively stronger than the carbonic acid produced by the action of the H ions. The use of sodium carbonate in washing powders depends upon the fact that its water solution acts like a base.

Zinc chlorid hydrolyzes slightly in water.

$$ZnCl_2 + 2HOH \stackrel{\rightarrow}{\longrightarrow} Zn(OH)_2 + 2HCl$$

Here the hydrochloric acid that is formed is relatively stronger than the weak base, zinc hydroxid. The solution turns blue litmus red. Its use in soldering depends upon its ability to act like an acid in water solution, thus dissolving oxids of metals.

Aluminum sulfid hydrolyzes almost completely in water.

$$Al_2S_3 + 6HOH \rightarrow 2Al(OH)_3 + 3H_2S$$

Both the acid and the base from which aluminum sulfid is formed are very weak. The hydrogen sulfid that is liberated escapes as a gas, while the aluminum hydroxid is thrown down as a precipitate.

#### SUMMARY

Reactions run to completion: (1) if an insoluble compound is formed; (2) if a volatile product is liberated; (3) if a compound is formed that does not dissociate

Reactions run to equilibrium when none of the products formed are removed from the field of action by insolubility, volatility, or undissociation.

By changing the concentration of the constituents it is possible to force a chemical reaction in a certain direction.

Hydrolysis is the decomposition of a compound, especially a salt, by the action of water.

Almost no hydrolysis occurs when both the acid and the base from which the salt was formed are very strong.

When either the acid or the base is weak some hydrolysis occurs; if the former is strong and the latter weak the solution of the salt in water acts like an acid, and conversely.

Practically complete hydrolysis occurs when the salt of a very weak base and a very weak acid is dissolved in water.

#### **QUESTIONS**

- 1. Write the equations given in Chapter XV, showing which ones run to completion and which to equilibrium. Give the reasons.
- 2. From your knowledge of soap, would you expect its solution to react acid or alkaline?
- 3. Why is a knowledge of *physical* chemistry so important to manufacturing chemists?

#### CHAPTER XXIII

## CARBON

- 213. Occurrence of Carbon.—Under the study of fuels we learned that coal, wood, and oils contain carbon. This element is not only a constituent of fuels, but all plants and animals contain carbon. Its presence may be shown by the black color produced whenever organic matter is charred.
- 214. Allotropic Forms.—Like sulfur, carbon also exists in three allotropic modifications: (a) amorphous carbon, of which charcoal, coke, lamp-black, bone-black, and gas carbon are examples; (b) graphite; (c) diamond.
- 215. Charcoal.—Charcoal is prepared by the destructive distillation of wood. The wood is heated in retorts; combustible gases, wood vinegar or acetic acid, and wood alcohol are among the by-products obtained, while charcoal is left in the retort as a residue.

Charcoal is a porous, black, brittle solid. It is heavier than water, although it often absorbs so much gas that it floats on water. For example, 1 volume of charcoal may absorb 90 volumes of ammonia gas. Charcoal, like other forms of carbon is insoluble in all ordinary solvents. At the temperature of the electric arc carbon volatilizes.

Chemically charcoal is inert at the ordinary temperature. Its most important chemical property depends upon the fact that it unites readily with oxygen at higher temperatures. Thus it is an excellent reducing agent.

Charcoal is used to absorb gases from liquids and thus

serves as a deodorizer; it is also used to decolorize certain liquids; it finds limited use as a fuel and a reducing agent.

216. Coke.—Coke is made by the destructive distillation of soft coal. A few years ago the bee-hive oven was largely used in this country. This oven is filled with coal, a part of which burns in a limited supply of air, furnishing enough heat to drive off the volatile matter from the unburned portion. The by-products, gas, coal-tar, and ammonia, are all wasted. It is estimated that the waste in 1913 of these by-products amounted to more than \$70,000,000. To save these by-products, which are worth about \$1.50 per ton of coal used, by-product coke ovens are now being rapidly installed to take the place of the older type. They also increase the yield of coke by 10 or 15 per cent.

Coke is a gray solid, harder and denser than charcoal. It burns readily and is an excellent reducing agent, enormous quantities being used every year in extracting metals from their ores.

- 217. Gas carbon is finely divided carbon that collects on the walls of the retorts used in making coal gas. When it is scraped off and pressed into sticks it becomes a good conductor, and finds extensive use for the carbons of arc lamps and for making the positive plate of dry cells.
- 218. Animal charcoal is made by the destructive distillation of bones. Calcium phosphate which is present to the extent of 80 per cent. or more is removed by treating the charcoal with hydrochloric acid.

Animal charcoal is used extensively for clarifying and decolorizing liquids, especially crude sugar solutions and oils.

219. Lamp-black.—When oil or gas is burned in an insufficient supply of air, soot or lamp-black is formed. In making lamp-black commercially the carbon is deposited on the cool surface of a revolving disc and then scraped off into bags.

Lamp-black is a velvety powder; it is used as a pigment, in making printer's ink, India ink, and shoe polish.

220. Graphite.—Graphite is a crystalline variety of carbon. It is soft, friable, and has a greasy feel. Its specific weight is 2.25. Graphite is a good conductor of electricity. Heated in oxygen to a high temperature it burns forming carbon dioxid. The best graphite comes from Ceylon and Siberia although it is found in many other localities, among which are Austria, Germany, Canada, and the United States. Artificial graphite is now being made by heating hard coal or coke in an electric furnace.

Since graphite breaks up into small scales that readily slide over one another it is used as a *lubricant*, especially where the temperature is high enough to decompose oils. Very finely divided (deflocculated) graphite forms an emulsion with water or oil and thus makes an excellent lubricant. Graphite is sometimes used in smokeless powders to prevent gun erosion. Hard water does not form so hard a boiler scale when graphite is introduced into the boiler.

Graphite is used as an electrical conductor in electrotyping and also for the preparation of electrodes.

Since graphite is very refractory it is used in making crucibles. For use in making steel the graphite is sometimes mixed with clay to form the crucible.

Graphite is often called black lead. It is used in making lead pencils. The hardness of the pencil depends upon the amount of clay that has been mixed with the graphite.

221. Diamond.—The diamond is also a crystalline form of carbon. It is the densest form of carbon, its specific weight being 3.5. It is one of the hardest substances known. When burned in oxygen it forms nothing but carbon dioxid, hence it is composed of pure carbon.

The value of the diamond as a gem depends upon its color and its high index of refraction, which is nearly 2.5. It is so cut that its brilliance will be increased by the play

of colors from numerous facets. Low-grade diamonds are used for cutting very hard materials. The black diamond is used-extensively by mining prospectors. The diamond drill is fitted with a steel shoe set with black diamonds. In prospecting for ores, this drill cuts out a solid core which is brought to the surface for examination. The carat is the weight unit used in the sale of diamonds. It is equal to 200 milligrams.

222. The Electric Furnace.—In its simplest form the electric furnace consists of two carbon rods mounted in a block of refractory material (see Fig. 71). The carbon

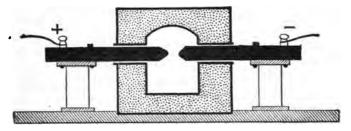


Fig. 71.—A simple electric furnace.

electrodes are brought together momentarily. At the point of contact the heat developed volatilizes the carbon, its vapor conducting the current as the rods are slightly separated. The temperature is exceedingly high, estimated at 3500°C. A large number of chemical reactions occur at this temperature that can not be brought about in any other way. The changing of hard coal into graphite when heated in the electric furnace has already been mentioned. Carbon disulfid is another compound we have studied that is made in an electric furnace. Calcium carbid is made by heating a mixture of quick-lime and coke in the electric furnace,

$$CaO + 3C \longrightarrow CaC_2 + CO.$$

Carborundum, CSi, is another product of the electric furnace; it is made from sand and coke.

Moissan succeeded in preparing artificial diamonds by the use of an electric furnace. By dissolving carbon in molten iron in an electric furnace and then cooling the surface quickly the shrinkage produces enormous pressure. Under such pressure the carbon crystallizes from its solution to form minute diamonds. The process is of no commercial value.

### SUMMARY

Carbon is present in the air in the form of carbon dioxid; it occurs in all organic matter, both plant and animal.

Carbon exists in three allotropic forms: amorphous carbon, graphite, and the diamond.

Charcoal, coke, gas carbon, bone-black, and lamp-black are all varieties of amorphous carbon.

Charcoal is prepared by the destructive distillation of wood, bone-black by the destructive distillation of bones, and coke by the destructive distillation of soft coal.

At the ordinary temperature all forms of carbon are inert; at higher temperatures they unite with oxygen to form carbon monoxid or the dioxid.

Carbon absorbs gases readily and hence deodorizes solutions; it also decolorizes certain solutions. Since it is insoluble in ordinary solvents it makes a good pigment, being used for paints or lacquers and for inks.

The electric furnace has recently come into quite extensive use for producing very high temperatures. It is used for making artificial graphite, calcium carbid, and carborundum.

# QUESTIONS AND PROBLEMS

- 1. Why is it so difficult to remove stains made by printer's ink?
- 2. Why is carbon one of the most important elements?
- 3. Bags of charcoal are often attached to water faucets. How may these become a source of danger rather than a protection?

- 4. What properties has graphite that make it useful for stove polishes?
- 5. Why does a kerosene lamp often burn with a smoky flame? Suggest at least two remedies.
- 6. Is the name "lead pencil" a good one? Give a reason for your answer.
- 7. How many pounds of air will be required for the complete combustion of 1 ton of 98 per cent. charcoal?
- 8. Name as many products as you can that are made in the electric furnace.
- 9. Why are the ends of telegraph poles often charred before being put in the ground?

Topics for Reference.—Electrical industries at Niagara Falls. Moissan. Diamond cutting. Famous diamonds.

# CHAPTER XXIV

# OXIDS OF CARBON—ILLUMINATING AND FUEL GASES

#### CARBON DIOXID

- 223. Occurrence.—Carbon dioxid is found in the air, since it is exhaled by animals. It is also a product of all ordinary combustion; and it is often formed when plant and animal bodies decay.
- 224. Preparation.—There are several ways in which carbon dioxid may be prepared.
- 1. Burning Carbon.—When any one of the forms of carbon or any carbonaceous material burns, carbon dioxid is one of the products. When this method is used the gas is impure, being mixed with the constituents of the air and other products of combustion.
- 2. Heating · Carbonates.—When calcium carbonate is heated it decomposes as follows:

$$\begin{array}{c}
\uparrow \\
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2.
\end{array}$$

With the exception of the carbonates of sodium and potassium, this decomposition is characteristic of carbonates.

3. Action of Acids on Carbonates.—Since carbonic acid is a very weak acid, nearly all acids will decompose its salts readily.

$$\begin{aligned} \text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{CO}_3 \\ & & \uparrow \\ \text{H}_2\text{O} + \text{CO}_2. \end{aligned}$$
 
$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{CO}_3 \\ & & \downarrow \uparrow \\ \text{H}_2\text{O} + \text{CO}_2. \end{aligned}$$

The carbonic acid that is formed breaks up into water and carbon dioxid. The gas may be collected by water displacement, or by downward air displacement.

- 225. Properties, Physical.—Carbon dioxid is a colorless gas with a slight odor and taste. It is about 1½ times as heavy as air, and frequently collects at the bottom of wells, mines, and caves. Before entering dry wells workmen often lower a lighted candle to see whether sufficient carbon dioxid is present to extinguish the flame. If the gas is present it is bailed out with buckets before the workmen enter. It is not poisonous, but animals die in it from suffocation. It is soluble in water. The gas may be rather easily liquefied; liquid carbon dioxid is put on the market in steel cylinders.
- 226. Properties, Chemical.—Carbon dioxid is a stable compound. It neither burns nor supports combustion, although such metals as burning sodium or magnesium decompose it and continue to burn by uniting with the oxygen abstracted from the carbon dioxid.

It is the anhydrid of carbonic acid. This acid is very weak and exists in water solution only.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$
.

Carbon dioxid interacts with the solutions of bases to form carbonates.

$$2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}.$$

If we use calcium hydroxid (lime-water) the calcium carbonate forms a white precipitate. This reaction,

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O_1$$

forms a test for carbon dioxid. In a similar manner carbon dioxid unites with the oxids of some metals to form carbonates.

227. Uses of Carbon Dioxid.—1. Fire Extinguishers.—One type of fire extinguisher generates carbon dioxid rapidly

by the action of sulfuric acid on sodium bi-carbonate (see Fig. 72). The pressure of the gas forces a stream of water and carbon dioxid bubbles into the fire.

2. Carbonated Beverages.—Certain mineral waters are made effervescent by charging them with carbon dioxid under pressure. Effervescence occurs when the bottle is



Fig. 72.—Carbon dioxid fire extinguisher.

opened. Soda fountains are charged with carbon dioxid in the same manner. Since carbon dioxid is produced when sugar ferments, such beverages as champagne are charged with carbon dioxid during fermentation.

3. As a Leavening Agent.—Yeast causes sugar to ferment and carbon dioxid is liberated. As the bubbles of gas become entangled in the plastic dough they cause it to rise not only while they are being set free but also when they are heated during the baking.

There are several ways of liberating the carbon dioxid. Baking soda is a carbonate. The carbon dioxid is evolved when soda is treated with sour milk, molasses, or cream of tartar.

Baking powders contain soda, starch, and some acid or acid salt. The starch

keeps the powder dry, while the soda furnishes the carbon dioxid. The compound used to set the carbon dioxid free varies with the kind of baking powder. Some use tartaric acid and cream of tartar; others use calcium acid phosphate; while a third type of powder uses alum. The alum hydrolyzes and acts like an acid.

4. As a Plant Food.—The use of carbon dioxid by plants in the manufacture of starch has already been discussed.

#### CARBON MONOXID

228. Preparation.—1. Burning Carbon in an Insufficient Supply of Air.—We have seen that carbon dioxid is formed when carbon burns in air or oxygen; if there is not enough oxygen, however, the combustion is incomplete and carbon monoxid is formed:

$$2C + O_2 \rightarrow 2CO.$$

2. Reduction of Carbon Dioxid.—When carbon dioxid comes into contact with white hot carbon it is reduced as follows:

$$CO_2 + C \rightarrow 2CO.$$

Both these methods of preparing carbon monoxid are used on a large scale in the extraction of metals from their ores.

3. Decomposition of Oxalic Acid (Usual Laboratory Method).—When oxalic acid, (COOH)<sub>2</sub>, is heated with sulfuric acid it breaks up as shown below:

The sulfuric acid dehydrates the oxalic acid which then splits up into carbon dioxid and carbon monoxid. This mixture may be separated by bubbling the gases through a solution of a base such as the hydroxid of sodium or calcium; the carbon dioxid unites with the base while the monoxid is unaffected and may be collected by water displacement:

$$H_2C_2O_4 \rightarrow H_2O + CO + CO_2.$$

229. Physical Properties.—Carbon monoxid is a color-less, odorless, tasteless gas. It is slightly lighter than air, having the same density as nitrogen. Carbon monoxid is very slightly soluble in water.

- 230. Chemical Properties.—Carbon monoxid burns with a blue flame. The burning gas from hard coal consists largely of carbon monoxid. It is very poisonous since it unites with the red blood cells and makes them unable to carry oxygen. As small an amount as 0.1 per cent. is dangerous to life, and rapidly produces fatal results. It finds its way into the air when coal burns in a limited amount of air; it is also one of the waste products from a gas engine. It is very dangerous to work about an automobile when the motor is running unless there is a good current of air to carry away the exhaust gases. The most important chemical property of carbon monoxid is its action as a reducing agent.
- 231. Uses.—Carbon monoxid has two very important uses: (1) As a reducing agent; (2) as a fuel.

In extracting metals from their ores the coke, charcoal, or coal forms carbon monoxid. The monoxid unites with the oxygen of the ore to form carbon dioxid and the metal. With copper oxid the reaction is as follows:

$$CuO + CO \rightarrow Cu + CO_2$$
.

Unless the carbon monoxid that forms in the burning of hard coal is oxidized, more than half the fuel value is wasted. Carbon monoxid is present to some extent in coal gas and it forms one of the chief constituents of water gas and producer gas.

## FUEL GASES AND ILLUMINATING GASES

232. Coal Gas.—Coal gas is made by heating soft coal in retorts. The retorts, R, are usually arranged one above the other to economize fuel. Fig. 73 shows the arrangement of a plant for making coal gas. From the retorts the gas passes through a dip-pipe into the hydraulic main, H; next it goes to the condenser, C, where it is cooled considerably

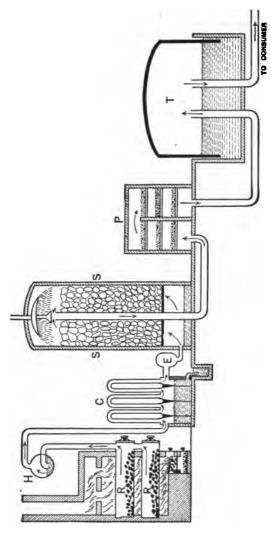


Fig. 73.—Diagram of a plant for making coal gas.

and the tar and ammonia partially removed. An exhauster, E, keeps the gas moving in the proper direction and regulates the pressure in the retorts. In the scrubbers, S, the traces of tar are mechanically removed and the gas thoroughly washed by a spray of water. In the purifiers, P, layers of lime or iron oxid, or sometimes both, are used to remove sulfur compounds and carbon dioxid. The purified gas then passes to a storage tank, T.

From a ton of good gas coal about 10,000 cu. ft. of gas, 1200 to 1400 lbs. of coke, 120 lbs. of coal tar, and 20 gal. of ammoniacal liquor are obtained. The constituents of the gas are shown in the table following gases.

233. Water Gas.—When steam comes into contact with white hot coke or hard coal, hydrogen and carbon monoxid are formed.

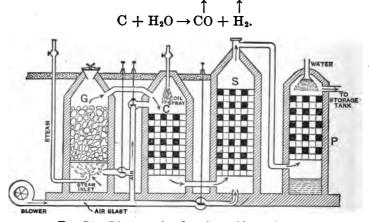


Fig. 74.—Diagram of a plant for making water gas.

Water gas is made commercially by forcing a blast of hot air through coal or coke until it is heated white hot. The air blast is then shut off and steam passed through the coke to form the hydrogen and carbon monoxid. Air and steam are then used alternately. Since both hydrogen and

carbon monoxid burn with little color, the water gas must be enriched if it is to be used for illuminating purposes. As the water gas comes from the generator, G, Fig. 74, it enters the carburetor, C. Here a spray of oils containing hydrocarbons is introduced. The mixture of these oils with the gas then enters the superheater, S, which blends them so the oils do not condense to a liquid when the gas is stored. Probably some of the oils in passing through the superheater are "cracked" or broken up into simpler, moregaseous, molecules. After passing through the lime purifiers, P, the gas goes to the storage tank.

Water gas has a high heat value. When enriched it forms a good illuminating gas. The high percentage of poisonous carbon monoxid forms the chief objection to its use. The impurities consist of ammonia, hydrogen sulfid, and carbon dioxid, the same as those found in coal gas.

- 234. Producer Gas.—A very cheap fuel gas is made by forcing a blast of hot air through hard coal or coke. Although it contains about 60 per cent. nitrogen, yet it burns with a very hot flame. Large quantities of producer gas are used in making steel, glass, pottery, etc.
- 235. Oil Gas.—1. Pintsch Gas.—In this process the less volatile portions of crude oil are heated to a high temperature, about 1000°C., to "crack" the molecules and form permanent gases. Pintsch gas is compressed and sold in steel containers. It is used to some extent for lighting railway coaches.
- 2. Blaugas is also an oil gas. In this process the oil is not heated over 550° to 600°C. in order to avoid "cracking" the molecules. After the gas is washed and purified in the usual manner, it is subjected to a pressure of nearly 100 atmospheres. Under this high pressure some of the hydrocarbons liquefy; others that are more gaseous remain dissolved in the liquid hydrocarbons as long as the high pressure is maintained. These liquid hydrocarbons are

delivered to the consumer compressed in strong steel cylinders. When the valve, V, is opened the hydrocarbons vaporize and enter an expansion tank which is placed under-

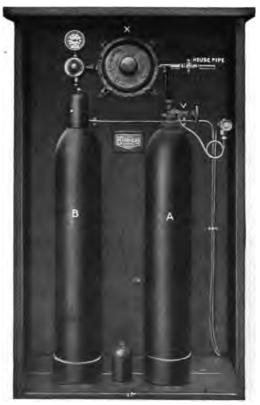


Fig. 75.—Blaugas cylinders. Pipe at right leads to underground expansion tank.

ground as shown in Fig. 75. In this expansion tank the gas is under a pressure of about 50 lb. to the square inch. Before it is delivered to the burners it passes through a second reducing valve, X, to lower the pressure to about

 $\frac{1}{2}$  lb. per square inch. Blaugas gives a luminous flame. It has a high heat value, and its explosive range is lower than that of most gases.

It is especially suitable for use in rural districts where connection with the city gas supply is impracticable.

236. Acetylene.—Acetylene is prepared by the interaction of water and calcium carbid.

$$\uparrow \\
CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2.$$



Fig. 76.—Welding with oxy-acetylene blow-pipe. A completed weld shown at the right.

Acetylene generators of sufficient size to supply dwelling houses and stores are now manufactured. The carbid is dropped into the water with sufficient rapidity to secure a steady evolution of the gas. Acetylene is a colorless gas with a peculiar odor. Unless a special burner is used it

burns with a smoky flame. With the burner of Fig. 31 an intense white flame similar to sunlight is produced.

Since the formation of acetylene is an endothermic reaction, more heat can be produced by burning acetylene than is yielded by the combustion of an equal weight of the elements of which it is composed. Not only the heat formed by oxidizing the carbon and hydrogen, but also the heat liberated by decomposing the gas, is available when it

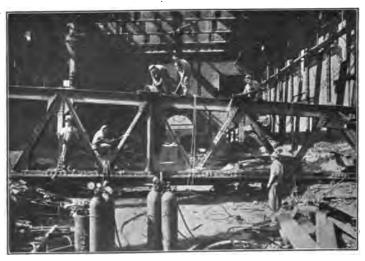


Fig. 77.—Cutting steel with the oxy-acetylene blow-pipe. Portable outfit shown in the foreground.

burns. The hottest flame that can be produced is made by using the oxy-acetylene blowpipe, a temperature of 2700°C. to 3500°C. being produced. This blowpipe is used for welding, Fig. 76, and for cutting wrought-iron and steel plates or scrap of any kind (Fig. 77). The tip of the flame is so hot that when it is drawn over the metal, it melts and burns the material in its path. It has been used by divers in cutting up submerged wrecks.

Since heat is absorbed when acetylene is formed, the gas may explode without oxygen. This may occur only when the gas is compressed. Acetylene also forms acetylids with metals, especially copper, which are explosive.

Prest-O-lite, used so extensively in lighting automobiles,

consists of a solution of acetylene in acetone. The tank is filled with asbestos which is soaked with acetone and the acetylene is then forced in under pressure (Fig. 78).

237. Explosion of Gases and Explosive Range.—Every one knows that a mixture of gasoline vapor and air explodes when ignited. Kerosene vapor also explodes when mixed with air, although in an open vessel it burns quietly. A mixture of 3 per cent. of acetylene and 97 per cent. air explodes when ignited. In fact any mixture of acetylene and air containing from 3 per cent. to 30 per cent. acetylene is explosive. Thus acetylene has quite a wide explosive range.



Fig. 78.— Prest-O-lite tank. (Sectional.)

Hydrogen has a wide explosive range, any mixture of hydrogen and air containing from 10 to 66 per cent. of hydrogen exploding violently. The explosion is most violent when the mixture contains 29 per cent. of hydrogen

Analysis of Gases (C. D. Jenkins, Mass. State Reports)

	Coal gas	Water gas (enriched)	Water gas	Oil gas
Candle-power	17.5	25		65
Illuminants	5	16.6		45
Marsh gas	34.5	19.8	1.0	38.8
Hydrogen	49	32.1	52	14.6 Ethane
Carbon monoxid	7.2	26.1	38	
Nitrogen and carbondioxid	4.3	5.4	9.0	1.1

For determining candle-power 5 cu. ft. of gas are burned per hour.

238. Cyanogen and Cyanids.—Cyanogen is a colorless gas that burns with a blue flame. It may be prepared by heating cyanids, such as mercuric cyanid,  $Hg(CN)_2$ . Its formula is  $C_2N_2$ . The gas is exceedingly poisonous.

Hydrogen cyanid, HCN, is a volatile liquid boiling at 26°C. Its water solution is called *prussic acid* or *hydrocyanic acid*. It is one of the most poisonous substances known. Its vapor finds some use in destroying insects. Its most important salts are the *cyanids of potassium and sodium*. These compounds find extensive use in extracting gold from its ores, and in electroplating.

# SUMMARY

Carbon dioxid may be prepared by burning carbon, by heating carbonates, or by the action of an acid on a carbonate.

Carbon dioxid is a heavy, colorless gas, fairly soluble in water. Its water solution forms carbonic acid. Carbon dioxid is stable; it neither burns nor supports combustion.

Carbon dioxid is used: (1) in carbonated waters; (2) as a leavening agent; (3) as a plant food; (4) to extinguish fires.

Carbon monoxid is a reduction product of carbon dioxid; it may be prepared by the incomplete combustion of carbon; or by heating oxalic acid with sulfuric acid.

It is colorless and odorless; it is intensely poisonous. Carbon monoxid burns with a blue flame. It is an excellent reducing agent.

Fuel and illuminating gases are made by the destructive distillation of soft coal and oil; water gas is made by blowing steam through hot coke; and acetylene gas by the action of water on calcium carbid.

At high temperatures nitrogen combines with carbon to form cyanogen, a very poisonous gas. With hydrogen, hydrocyanic acid is formed.

# **QUESTIONS AND PROBLEMS**

- 1. Can kerosene be substituted for gasoline to be used in gas engines? Give a reason for your answer.
- 2. Why should the engine not be left running when a car stands in a garage?
- 3. Write the equation for the complete combustion of acetylene. How many liters of oxygen are needed to combine with 12 liters of acetylene?
- 4. How many grams of sodium bi-carbonate, HNaCO<sub>3</sub>, will be needed to liberate 10 liters of carbon dioxid?
- 5. Suppose you were given samples of the following gases: oxygen, hydrogen, carbon dioxid, carbon monoxid, nitrogen, and nitrous oxid. How would you identify each?
- 6. Is it necessary to enrich water gas with oils if it is to be used for fuel only? If it is to be used for illumination with a Welsbach mantle?
- 7. Formic acid has the formula HCOOH. What gas would you expect to be formed when formic acid is heated with sulfuric acid?
- 8. Try to find a reason for using hydrochloric acid in preference to sulfuric acid in preparing carbon dioxid.
  - 9. Devise a test for a carbonate.
- 10. Why is water gas more dangerous when inhaled than coal gas?
- 11. A stick of sodium hydroxid slowly changes to a white powder when exposed to the air. What change is taking place?
- 12. When a bottle of lime-water is left unstoppered, a white ring is formed on the bottle at the surface of the liquid. Explain. How would you clean such a bottle?
- 13. Name the most important reducing agents that we have studied.

### ·CHAPTER XXV

# HALOGEN FAMILY

239. The Halogen Family.—Four elements, fluorin, chlorin, bromin, and iodin comprise this group. Their chemical properties are very similar and the method of preparing the elements as well as their acids is analogous. The word halogen means salt-producer.

#### CHLORIN

- 240. Occurrence.—Chlorin does not occur free in nature. It is found in chlorids, especially those of sodium and potassium. Magnesium chlorid is also fairly abundant.
- 241. Preparation.—1. Electrolysis.—Commercially chlorin is prepared by the electrolysis of a solution of sodium chlorid. The chlorin is set free at the anode, and the sodium which is liberated at the cathode unites with the water to form sodium hydroxid. The by-product is sodium hydroxid. If fused sodium chlorid is electrolyzed, metallic sodium and chlorin are the products obtained.
- 2. Oxidation of Hydrogen Chlorid.—If we treat hydrogen chlorid with an oxidizing agent, such as manganese dioxid, MnO<sub>2</sub>, the hydrogen of the acid is oxidized to water, manganese chlorid is formed, and chlorin is liberated. In the equation,

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2,$$

we note that the valence of the manganese changes from 4 to 2 during the reaction.

Since hydrogen chlorid is formed by the action of sulfuric acid on sodium chlorid, chlorin may be prepared by adding an oxidizing agent to a mixture of these compounds. The equation may be written in two steps,

$$2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$$

$$\uparrow$$

$$\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2,$$

or it may be combined in one equation as follows:

$$2\text{NaCl} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow$$

$$\begin{array}{c}
 \uparrow \\
 \text{Na}_2\text{SO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2.
 \end{array}$$

- 242. Properties, Physical.—Chlorin is a greenish-yellow gas about  $2\frac{1}{2}$  times as heavy as air; it has a very disagreeable suffocating odor. When inhaled in small quantities it attacks the mucous membrane of the nose and throat producing the same effect as a heavy cold. In larger quantities it produces death. The effects from breathing chlorin are partially alleviated by inhaling alcohol or ammonia. Chlorin is fairly soluble in water, imparting to the solution a pale yellow color.
- 243. Properties, Chemical.—1. Action with Metals.—If we sprinkle powdered antimony into a jar of chlorin, the two elements combine spontaneously to form antimony tri-chlorid. The action is so energetic that heat and light are evolved. Other metals, such as copper, zinc, iron, and arsenic, also combine directly with chlorin, especially if heated slightly.
- 2. Action with Hydrogen.—A mixture of hydrogen and chlorin in direct sunlight explodes violently. These elements combine more slowly in diffused daylight. Chlorin does not support ordinary combustion, but if a candle is lighted and thrust into a jar of chlorin it continues to burn emitting a smoky flame. The hydrogen of the candle

wax unites with the chlorin to form hydrogen chlorid and the carbon is set free. If a strip of filter paper is moistened with warm turpentine and suspended in chlorin, it bursts into flame, hydrogen chlorid being formed and the carbon of the turpentine liberated as a dense black soot.

$$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C.$$

Thus we see that chlorin nct only combines directly with hydrogen to form hydrogen chlorid but it has the ability to abstract hydrogen from compounds.

3. Action with Water.—When chlorin water stands in sunlight the chlorin gradually takes the hydrogen from the water to form hydrogen chlorid and oxygen is liberated.

$$H_2O + Cl_2 \rightarrow 2HCl + (O).$$



Fig. 79.—Bleaching effect of chlorin.

The nascent oxygen which is liberated by this decomposition of the water attacks coloring matter oxidizing it to form colorless compounds. Thus chlorin acts as a bleaching agent. Since a substance must be wet to be bleached by chlorin it is quite evident that the bleaching action depends upon the nascent oxygen and is an oxidizing process. In

the laboratory chlorin water is sometimes used as an oxidizing agent. Some dyes are not affected by chlorin but the natural yellow color of fibers is readily destroyed (see Fig. 79).

244. Uses of Chlorin.—1. As a Bleaching Agent.—For use in bleaching, chlorin is usually obtained from bleaching powder or chlorid of lime. This compound is prepared by passing chlorin gas into calcium hydroxid.

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O.$$

No definite formula can be given to this compound but it appears to be a salt of hydrochloric and hypochlorous acids closely corresponding to the formula CaOCl<sub>2</sub>. Chlorin is

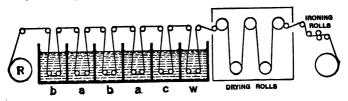


Fig. 80.—Commercial method of bleaching cotton goods.

easily liquefied and is sometimes transported in metal cylinders. In a new bleaching process an electric current is passed through a solution of sodium chlorid, the article to be bleached being attached to the anode.

Fig. 80 shows a common method used in bleaching cotton goods. To remove the wax from fibers that are to be bleached, a preliminary treatment is necessary. This consists in boiling the cloth with very dilute caustic soda or with sodium carbonate. From the roll, R, the goods are drawn through a vat, b, containing bleaching powder and water; they then go into a sulfuric acid vat, a, where hypochlorous acid, HClO, is liberated by the action of the acid on the bleaching powder, as in the following equation:

$$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + HCl + HClO.$$

As the HClO decomposes nascent oxygen is set free, acting as the bleaching agent. The cotton strip then passes through a second vat containing bleaching powder and then a second acid vat. Since any excess chlorin slowly destroys the fiber, an *antichlor* is used in vat c to remove the last traces of chlorin. The strip is then washed, ironed, and re-rolled.

- 2. As a Disinfectant.—Since moist chlorin is a good oxidizing agent in the presence of organic matter, bacteria are readily destroyed by it. Large quantities of "chlorid of lime" are used as a disinfectant. Large quantities of liquid chlorin are used for purifying city water supplies.
- 3. For Chlorin Compounds.—Large quantities of chlorin are used in making chlorin compounds. Carbon tetrachlorid is an example. This compound is used largely as a cleaning agent and for extinguishing fires.
- 4. In Warfare.—Chlorin has been extensively used in modern warfare as a poisonous gas. Since it is so much heavier than air it may be carried to considerable distances by the wind, without rising far from the earth's surface. Masks containing ordinary "hypo" are quite efficient in destroying the gas, so soldiers employed in the trenches are equipped with such a mask covering the nose and mouth.

## HYDROGEN CHLORID

245. Preparation.—Hydrogen chlorid is prepared by the action of sulfuric acid on sodium chlorid.

$$\uparrow 2NaCl + H2SO4 \rightarrow Na2SO4 + 2HCl.$$

The gas may be collected by the downward displacement of air or by dissolving it in water.

246. Properties, Physical.—Hydrogen chlorid is a colorless gas with a sharp, penetrating odor. It is heavier than air and dissolves readily in water, 1 volume of water absorbing about 500 volumes of the gas at standard conditions. The gas fumes strongly in moist air.

- 247. Chemical Properties.—1. Stability.—Hydrogen chlorid is a stable compound. It neither burns nor supports combustion, although some oxidizing agents attack it forming water and liberating chlorin.
- 2. As an Acid.—In water solution hydrogen chlorid forms hydrochloric acid. Concentrated hydrochloric acid contains about 38 per cent. of the gas by weight. If the solution is boiled hydrogen chlorid escapes until the solution contains only 20 per cent. of gas by weight; but when a more dilute solution is boiled water is given off and the solution becomes more concentrated until a 20 per cent. solution is formed. A 20 per cent. solution of hydrogen chlorid in water boils at 120°C. and its strength remains constant. Hydrochloric acid is one of the strongest acids known. It interacts with metals, oxids of metals, and bases to form chlorids.
- 248. Uses.—Hydrochloric acid is used in preparing chlorids, in making chlorin for the preparation of bleaching powder, and in cleaning metals.
- 249. Aqua Regia.—If we mix nitric acid and hydrochloric acid, aqua regia is formed. Such metals as gold and platinum, which are not affected by ordinary acids, dissolve in this mixture. The chemical action is due to nascent chlorin. Nitric acid is a strong oxidizing agent, oxidizing the hydrochloric acid and liberating the chlorin. Since it is the chlorin thus set free in the nascent state that attacks the metals, chlorids are formed by dissolving metals in aqua regia. The most common proportion consists of 1 part of nitric acid to 3 parts of hydrochloric acid, although other proportions are often used.
- 250. Chlorids.—The chlorids form an important class of salts, since chlorids of all metals are known as well as the chlorids of many non-metals. In general chlorids are crys-

talline solids. All common chlorids are water soluble except the chlorids of lead, silver, and mercurous mercury.

251. Oxygen Acids of Chlorin.—Chlorin forms several acids containing oxygen. All were mentioned as illustrations of the method of naming acids. The acids themselves are quite unstable and unimportant but some of them form important salts, especially the chlorates and hypochlorites.

# **BROMIN**

- 252. Occurrence.—Several bromids are found in nature, the most abundant being bromids of sodium and magnesium. The chief source of bromin is the "mother liquor" from salt wells after the salt has been extracted. Bromids are also found in the deposits at Stassfurt, Germany.
- 253. Preparation.—The method of preparing bromin is analogous to that of making chlorin. A bromid is treated with sulfuric acid and the hydrogen bromid formed is oxidized with manganese dioxid.

$$2KBr + H2SO4 \rightarrow K2SO4 + 2HBr.$$

$$\uparrow$$

$$4HBr + MnO2 \rightarrow MnBr2 + 2H2O + Br2.$$

As in the case of chlorin the equations may be combined as follows:

$$2KBr + MnO_2 + 2H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + 2H_2O + Br_2.$$

Commercially bromin is often prepared by decomposing bromids with chlorin:

$$\begin{array}{c} \uparrow \\ \mathrm{MgBr_2} + \mathrm{Cl_2} \, \rightarrow \, \mathrm{MgCl_2} + \mathrm{Br_2}. \end{array}$$

254. Physical Properties.—Bromin is a dark red liquid about three times as heavy as water. It is quite volatile; its vapor has a very disagreeable odor and it irritates the

eyes and throat. If the liquid comes into contact with the skin it produces frightful burns. Bromin is moderately soluble in water forming a reddish-brown solution.

- 255. Chemical Properties.—Bromin resembles chlorin in its chemical properties although it is less active. It unites with metals to form bromids. With hydrogen it forms hydrogen bromid. It is also a bleaching agent and its water solution is an oxidizing agent.
- 256. Uses of Bromin.—Bromin finds considerable use in making organic compounds, especially dye-stuffs. Sodium and potassium bromids are used in medicine as sedatives. Silver bromid is used extensively in photography.
- 257. Hydrogen Bromid.—Hydrogen bromid may be prepared by treating a bromid with sulfuric acid:

$$\uparrow
2KBr + H2SO4 \rightarrow K2SO4 + 2HBr.$$

Since hydrogen bromid is more unstable than hydrogen chlorid it is partially oxidized by the sulfuric acid. Thus some bromin is set free. Pure hydrogen bromid is prepared by the action of water on phosphorus tri-bromid:

$$PBr_3 + 3H_2O \rightarrow H_3PO_3 + 3HBr.$$

Hydrogen bromid is very similar to hydrogen chlorid in all its properties although it is less stable. It dissolves readily in water to form *hydrobromic acid*. The solution acts as a strong acid, forming bromids.

#### IODIN

- 258. Source.—Iodin was formerly obtained almost entirely from the ash left after burning kelp or sea-weeds. The chief source now is the nitrate beds of Chile.
- 259. Preparation.—Iodin is prepared in a manner analogous to that of obtaining chlorin and bromin. An iodid is

treated with sulfuric acid in the presence of an oxidizing agent:

$$\uparrow$$
 2KI + MnO<sub>2</sub> + 2H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$  K<sub>2</sub>SO<sub>4</sub> + MnSO<sub>4</sub> + 2H<sub>2</sub>O + I<sub>2</sub>.

- 260. Physical Properties.—Iodin is a steel-gray, crystal-line solid. When heated it sublimes, or vaporizes, without first liquefying. Its vapor which is violet in color has an irritating odor, somewhat resembling that of chlorin. Iodin is very slightly soluble in water. It dissolves readily in alcohol, forming the tincture of iodin. In an aqueous solution of potassium iodid it is very soluble and it dissolves very readily in carbon disulfid, giving a beautiful violet or purple solution.
- 261. Chemical Properties.—If we put a crystal of iodin on a piece of phosphorus the two elements combine spontaneously giving off heat and light. It also combines readily with other elements but it is less active than chlorin or bromin. With starch iodin combines to form a compound having a characteristic blue color; the reaction serves as a test for either starch or iodin.
- 262. Uses of Iodin.—Iodin is used in medicine, in photography, and for making dye-stuffs. The tincture of iodin is used as a counter-irritant to reduce swellings. Large quantities are now used to disinfect wounds.
- 263. Hydrogen iodid may be formed by the action of sulfuric acid on potassium iodid, but since it is less stable than hydrogen bromid it reduces a part of the sulfuric acid to hydrogen sulfid and some free iodin is liberated. The pure gas may be prepared by the action of water on phosphorous iodid:

$$PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI$$

It is a colorless gas very similar in its properties to hydrogen chlorid except that it is less stable. It dissolves in water forming hydriodic acid; this solution has all the characteristic properties of a strong acid, attacking metals, metallic oxids, and bases to form iodids.

#### FLUORIN

264. Fluorin.—Fluorin is the most active element known, combining readily with practically all the elements except oxygen. It resembles chlorin in its physical properties, but it is *more* active chemically. Fluorin combines explosively with hydrogen even in the dark. It attacks nearly all metals, gold and platinum *slowly*. It can not be prepared by oxidizing hydrogen fluorid, analogous to the preparation of the other halogens; the only method used for preparing the element is the electrolysis of a fluorid, usually potassium acid fluorid, KHF<sub>2</sub>.

265. Hydrogen fluorid is prepared by the action of sulfuric acid on calcium fluorid.

$$\begin{array}{c}
\uparrow \\
\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{F}_2
\end{array}$$

Like the other halogen compounds with hydrogen, it is a colorless gas that fumes strongly in moist air. It dissolves in water forming hydrofluoric acid. This acid is very corrosive, causing painful sores that heal very slowly. The vapor is very dangerous if inhaled. Hydrofluoric acid attacks most ordinary substances, wax, lead, and platinum being the most common exceptions. At the ordinary temperature the molecular weight of the gas is 40, showing that its formula is  $H_2F_2$ . At somewhat higher temperatures its molecular weight is only 20, corresponding to the formula HF.

The chief use of hydrofluoric acid is for etching glass. The glass is first covered with paraffin or wax; the paraffin is then removed with a sharp stylus from the part to be etched. This prepared glass is then exposed to the gas,

hydrogen fluorid, or covered with a solution of hydrofluoric acid (see Fig. 81) until the etching is of the required depth. The excess acid is then washed off and the paraffin removed. If a solution is used the etching is smooth and transparent; if the gas is used it will be more or less rough and translucent.



Fig. 81.—The word "chemistry" was etched with the gas hydrogen fluorid; the other words with a solution of the gas.

266. Relative Stability of the Halogen Compounds.—A study of the halogen compounds shows that the compounds of fluorin are the most stable; chlorin compounds are next in stability, followed by those of bromin; iodin compounds are least stable. These facts seem obvious if we consider the relative activity of the different elements. The heat of formation also varies as the following heat equations show. The amount of heat liberated is for the formation of 1 mole of the hydrogen compounds:

 $H + F \rightarrow HF$  plus 37,600 calories.  $H + Cl \rightarrow HCl$  plus 22,000 calories.  $H + Br \rightarrow HBr$  plus 8,400 calories.  $H + I \rightarrow HI$  minus 6,100 calories. In the preparation of hydrogen iodid at the ordinary temperature heat is absorbed, or the reaction is endothermic.

The fact that one halogen can replace another is also of interest as related to stability. If we add chlorin water to a solution of a bromid, the chlorin takes the place of the bromin as shown by the equation:

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$
.

We have seen that this reaction is of importance in the commercial preparation of bromin. In a similar manner chlorin replaces iodin; and bromin replaces iodin:

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$
.  
 $2KI + Br_2 \rightarrow 2KBr + I_2$ .

These reactions are exactly what we might expect from the heat equations shown above. The last reaction may be strikingly shown by making use of the greater solubility of both bromin and iodin in carbon disulfid as compared to water. The student should also bear in mind the fact that both bromin and iodin must be free to color carbon disulfid.

If we add to a water solution of potassium iodid a few drops of carbon disulfid and shake thoroughly, neither the water layer nor the carbon disulfid will be colored since combined iodin does not color its solutions. Now if we add a little bromin water and again shake the solution the carbon disulfid will be colored purple showing that the bromin has combined with the potassium and set free the iodin as represented in the equation above. Had the bromin remained free and dissolved in the disulfid a reddish-brown color would have been produced.

#### SUMMARY

Fluorin, chlorin, bromin, and iodin comprise the halogen group.

With the exception of fluorin, which is prepared by elec-

trolysis, the halogens are all prepared by oxidizing the hydrogen acids of the respective elements.

The hydrogen acids of the halogens may be prepared by treating a salt of the acid required with sulfuric acid.

Properties	Fluorin	Chlorin	Bromin	Iodin
Atomic weight	19	35.5	80	127
State	gas	gas	liquid	solid
Principal valence	1	1	1	1
Boiling point	−187°C.	−34°C.	59°C.	184°C.
Activity	most	less	still less	least
Formula of hydrogen acid.	$\mathbf{HF}$	HCl	HBr	HI
Stability of hydrogen acid.	most	less	still less	least
Heat of formation of hydrogen acid	37,600	22,000	8,400	-6,100
Replacement	replaces Cl, Br, and I	replaces Br and I	replaces iodin	

# QUESTIONS AND PROBLEMS

1. Balance and complete the following equations:

$$Cu + Cl \rightarrow$$
 $As + Cl \rightarrow$ 
 $Zn + Cl \rightarrow$ 

- 2. Compare the chemical action of chlorin, sulfur dioxid, ozone, and hydrogen peroxid as bleaching agents.
- 3. Can you see any advantage in having the bleaching powder and the sulfuric acid in separate vats in bleacheries?
- 4. Give two reasons why nitric acid is not suitable for use in making hydrogen chlorid.
  - 5. How would you test for free iodin? For combined iodin?
- 6. How many grams of chlorin are needed to displace the bromin in 100 grams of potassium bromid?
- 7. Why do solutions of hydrogen iodid become dark-colored on standing?
- 8. Why should chlorin water be kept in dark-colored bottles or in a dark place?

- 9. From the source used in obtaining bromin what do you judge concerning the relative solubility of chlorids and bromids?
  - 10. Why is hydrofluoric acid put on the market in wax bottles?
- 11. How would you test for the presence of a fluorid, a chlorid, a bromid, and an iodid?
- 12. What does the term "aqua regia" mean and why is a mixture of nitric and hydrochloric acids given this name?
- 13. How many grams of sodium chlorid are needed to prepare 40 grams of hydrogen chlorid? To prepare 40 liters of hydrogen chlorid? To saturate 1 liter of water at standard conditions?

Topics for Reference.—Moissan's work in preparing fluorin. The history of bromin and iodin.

# CHAPTER XXVI

# GROUPING OF ELEMENTS—PERIODIC LAW

267. Classification of Elements.—If the student of chemistry were to take up the study of each element as an individual, his task would become increasingly more difficult. In our study of hydrogen, oxygen, carbon, and nitrogen we did not find any marked relation between these elements. It is true that all are non-metallic, acid-forming elements. Elements have been classified as metallic and non-metallic: but there are some elements that are on the border line, having to some extent the properties of both the metals and the non-metals. Elements have also been classified as acid-forming elements and base-forming elements; but here again the classification is not very satisfactory since some elements may form amphoteric compounds that act as either acids or bases.

If we compare oxygen and sulfur we find that, in addition to being acid-forming elements, they have other chemical properties in common. Both are very active at higher temperatures. Both exist in allotropic modifications. Sulfids and oxids are very much alike in manner of formation, valence of the negative element, and solubility.

A much more striking resemblance may be noted in the halogen group of elements. So similar are these elements that it is possible to predict with reasonable accuracy the chemical behavior of one of them from the characteristic properties of the family or group. Attempts to classify elements show that it is possible to group other elements into families.

268. Mendelejeff's Periodic Law.—While many attempts to classify elements have been made, the work of Mendelejeff, a Russian chemist, has been the most successful. He believed that the chemical properties of elements are functions of their atomic weights.

Omitting hydrogen, suppose we arrange the elements in the order of their atomic weights, and examine the first eight.

Helium is an inert element; lithium is metallic, a very strong base former; beryllium is metallic, a base former; boron may form a base, although it more often forms a weak acid; carbon forms a weak acid; nitrogen forms strong acids; oxygen is characteristically acid; and fluorin is the most active non-metal known. Thus these elements form a series where the base-forming properties decrease and the tendency to form strong acids increases.

Now let us add to the above list the next eight elements, placing them in a new series below the first eight.

	Be 9			
	Mg 24			Cl 35.5

Like helium, neon is inactive; sodium is also a strong base former resembling lithium; magnesium is similar to beryllium; aluminum is like boron; like carbon, silicon is a weak acid-forming element; phosphorus resembles nitrogen in its chemical properties; sulfur is like oxygen chemically; and chlorin is very active like fluorin.

By arranging all the elements in the order of their atomic weights Mendelejeff discovered that the properties of the elements recur at regular intervals. He therefore concluded that the properties of elements are periodic functions

Period	Group 0 Group 1 A	Group 1 A B	Group 2 A B	Group 3 A B	Group 4 A B	Group 5	Group 6	Group 7	8	Group 8	
н	He (4)	3.6	Be (9.1)	B (11)	C (12)	N (14)	0 (16)	F (19)			
es .	Ne (20)	Na (23)	Mg (24)	A1 (27)	• Si (28)	P (31)	8 (32)	C1 (35.5)			
က	A (39.9)?	K (39.1) Cu (63.6)	Ca (40) Zn (65.4)	Sc (44.1) Ga (69.9)	Ti (48.1) Ge . (72.5)	V (51.2) As (75)	Cr (52) Se (79.2)	Mn (54.9) Br (80)	Fe (56)	Ni (58.7)	လို့ <u>(</u>
4	Kr (83)	Rb (85.5) Ag (107.9)	Sr (87.6) Cd (112.4)	Yt (89) In (114.8)	Zr (90.6) Sn (119)	Cb (93.5) Sb (120.2)	Mo (96) Te (127.5)	 I (127)	Ru (101.7) (	Ru Rh Pd (101.7) (102.9) (106.7)	Pd 106.7)
NG.	Xe (130.2)	Cs (132.8) Au (197.2)	Ba (137.4) Hg (200)	La (139) Ti (204)	Ce (140.2) Pb (207.1)	Ts (181) Bi (208)	.w (184)		Os Ir (190.5) (193.1)	Ir (193.1)	Pt (195)
Đ	Nt (222.4)		Ra (226.4)		Th (232.4)		U (238.5)				
Oxids		R <sub>2</sub> O RH	RO RH;	R,O, RH,	RO: RH4	R <sub>2</sub> O <sub>5</sub> RH <sub>3</sub>	RO, RH,	R <sub>2</sub> O, RH		RO4	



Robert Wilhelm Bunsen (1811-1899) was a German chemist. For nearly forty years he was professor of chemistry at the University of Heidelberg. He was the inventor of many laboratory devices, including the Bunsen burner, a photometer, a voltaic cell, a filter pump, and a thermostat. His most important work was his discovery, with Kirchhoff, of spectrum analysis. By this method elements are detected, and new ones have been discovered. Bunsen discovered caesium and rubidium.

Dimitri Ivanovitch Mendelejeff (1834-1907) was a Russian chemist born in Siberia. He was Professor of Chemistry at the University of St. Petersburg. His "Elements of Chemistry" is a standard work and has been translated into English, German, and French. His most important work was the Periodic Law which deals with the classification of elements.



	·	

of their atomic weights. If we refer to the complete table, page 236, we find that the recurrence of properties causes certain families of elements, like the halogens, to fall in the same group. Thus in group 0 we find all the inactive elements. In group 1 we find the alkali metals, lithium, sodium, potassium, caesium, and rubidium. The nitrogen family, including nitrogen, phosphorus, arsenic, antimony, and bismuth, is found in group 5.

After the first two series, the period is longer before the recurrence of properties occurs, eighteen elements comprising the third series. The following series are also made up of long periods. At the bottom of each group in the following table, a general formula for the oxids of the elements comprising that group is given, as well as a general formula for the hydrids.

- 269. Two Families in a Group.—In the foregoing table it will be seen that in the long periods there are two families in a group, A and B. The elements of family A, lithium, sodium, potassium, rubidium, and caesium, have properties similar to each other, but they are less like copper, silver, or gold, elements of family B in the same group.
- 270. Value of the Periodic Law.—1. It Simplifies Chemistry.—We have already seen that the grouping of elements into families makes the study of the properties and behavior of elements less difficult to grasp and retain.
- 2. It Serves as a Check on Atomic-weight Determinations.— When the periodic table was first prepared several of the elements were not properly placed. The suggestion that this might be due to errors in the atomic-weight determinations seemed plausible. More accurate methods were used, giving new values for certain atomic weights. Upon the substitution of these new values many elements then fitted into their proper places in the table. To illustrate, it appears that the atomic weight of argon may still be in error.

3. In the Prediction of New Elements.—There are several gaps in the table, which led Mendelejeff to predict the existence of undiscovered elements, having properties and atomic weights that make them fit into these gaps. In fact, within a few years immediately following the announcement of Mendelejeff's law several elements were discovered whose properties and atomic weights are very nearly in accord with what he had predicted. The remarkable agreement between the predicted properties of eka-aluminum and the actual properties of gallium are shown in the following table:

	Predicted	Discovered	
Atomic weight	About 69	69.9	
Melting point		30.2°	
Specific weight		5.95	
Formula of oxid		$Ga_2O_3$	
Action of air	None	Slight, even at red heat	

Since this element was discovered in France, it was named gallium. Mendelejeff also predicted the properties of *ekaboron* (scandium) and *eka-silicon* (germanium) with practically equal accuracy. Other elements, more recently discovered, have found places in the table.

#### SUMMARY

Elements are grouped as metals and non-metals; they are also classed as acid-forming elements and base-forming elements.

Mendelejeff arranged the elements in the order of their atomic weights. He then formulated the law that the properties of elements are periodic functions of their atomic weights.

The periodic law is of value: (1) in classifying elements and thus simplifying the study of chemistry; (2) it serves as a check upon the accuracy of atomic-weight determinations; (3) it indicates the presence of undiscovered elements in the earth's crust and has on several occasions enabled accurate predictions to be made concerning the properties and atomic weights of elements then undiscovered.

## QUESTIONS

- 1. If an element were discovered having an atomic weight less than copper and greater than cobalt, what properties would you expect it to have?
- 2. Write the formula for the oxid, hydroxid, sulfate, and carbonate of strontium.
- 3. Aluminum hydroxid is insoluble in water. What would you infer as to the solubility of the hydroxid of scandium?
  - 4. What properties would you expect caesium to have?

Topic for Reference.—Mendelejeff.

# CHAPTER XXVII

# THE NITROGEN FAMILY

271. Nitrogen Family.—Of the elements comprising the nitrogen family, five are of sufficient importance to be quite well known, namely: nitrogen, phosphorus, arsenic, antimony, and bismuth. Nitrogen has already been studied The acid-forming properties of the group decrease from nitrogen to bismuth, nitrogen forming very strong acids, while antimony and bismuth may act as base-forming elements in the presence of strong acids.

#### **PHOSPHORUS**

- 272. Occurrence.—The most important compounds of phosphorus found in nature are phosphates of calcium. The bones and teeth of animals contain calcium phosphate. This phosphate is present to some extent in all soils, and extensive areas of rock phosphate are found in Florida, Tennessee, and South Carolina, phosphorite and apatite being the most abundant.
- 273. Preparation.—Phosphorus is now extracted from calcium phosphate by heating this compound with sand and carbon in an electric furnace. Carbon monoxid is liberated by this reaction and the slag that is formed consists of calcium silicate. The phosphorus is purified by distillation.
- 274. Yellow Phosphorus.—Phosphorus exists in two important allotropic modifications; the white or yellow, and the red.

Yellow phosphorus is a waxy, translucent solid not quite twice as heavy as water. It is nearly colorless or a pale straw color. It melts at 44°C., but since its kindling temperature is only 35°C., it must be melted under water to prevent combustion. It is soft enough to be easily cut with a knife, but it should always be cut under water in order that the heat from the friction of the knife in cutting it does not cause it to be enkindled. Yellow phosphorus should never be touched with the hand since burning phosphorus produces wounds that are a long time in healing. It is very poisonous, even small quantities taken internally proving fatal. Although insoluble in water, yellow phosphorus dissolves readily in carbon disulfid.

Phosphorus oxidizes readily when exposed to the air, giving off dense white fumes of phosphorus pentoxid, P<sub>2</sub>O<sub>5</sub>. If this oxidation occurs in a dark room a faint glow or *phosphorescence* can be seen. To prevent oxidation phosphorus is always kept under water. In oxygen phosphorus burns with dazzling brilliancy. Heated to a temperature of 250°C. without access to air, or upon exposure to sunlight, it changes to *red* phosphorus.

275. Red Phosphorus.—This allotropic form of phosphorus is a dark red, amorphous powder. It is a little more than twice as heavy as water and insoluble in carbon disulfid.

Red phosphorus is not poisonous; it does not take fire when exposed to the air; its kindling temperature is about 250°C., phosphorus pentoxid being formed as it burns. When heated without access to air to a temperature of about 290°C., it sublimes and forms yellow phosphorus upon condensation.

276. Uses.—Some phosphorus is used as a poison for destroying rats and other vermin. Small quantities find use in making special alloys with bronze that are not corroded by water. Large quantities of phosphorus are used in the match industry.

277. Matches.—The old friction match was tipped with yellow phosphorus. So many workmen in match factories contracted a disease producing decay of the jaw-bones from the inhalation of phosphorus vapors, and so many children were poisoned by sucking the phosphorus from the matches themselves that a law was passed in 1913 taxing these matches out of existence (2 cents per 100 matches).

Two types of matches are now in common use: (1) the friction match; (2) the safety match. In the manufacture of the first type the stick is now dipped into molten paraffin, or in a few cases into sulfur, and then into a paste that has three constituents: (1) phosphorus sesquisulfid  $(P_4S_3)$ ; (2) an oxidizing agent; (3) some binding material such as glue.

The head of the ordinary safety match consists of antimony trisulfid, Sb<sub>2</sub>S<sub>3</sub>, some oxidizing agent such as potassium chlorate, and glue. The box is covered with a layer of red phosphorus, powdered glass, and glue. Such matches do not readily ignite except by rubbing them on this preparation on the box. The wood is usually impregnated with a fireproofing material to prevent after-glow.

- 278. Phosphine.—By indirect methods phosphorus may be made to combine with hydrogen to form phosphine,  $H_3P$ , a compound analogous to ammonia. Like ammonia it also unites with another hydrogen atom in forming phosphonium compounds having the  $H_4P$  radical.
- **279.** Oxids of Phosphorus.—Two oxids of phosphorus are known: phosphorous oxid,  $P_2O_3$ , is formed when phosphorus burns in a limited supply of air; phosphoric oxid,  $P_2O_5$ , a white solid, is formed when phosphorus burns in air or oxygen. This oxid has a great affinity for water and does not combine readily with many gases, hence it is used extensively for drying gases.
- 280. Acids of Phosphorus and Their Salts.—Of several acids of phosphorus, ortho-phosphoric acid, H<sub>2</sub>PO<sub>4</sub>, is the

most important. It may be formed by dissolving phosphoric oxid, its anhydrid, in water, but it is usually prepared commercially by the action of sulfuric acid on a phosphate.

$$2Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$$

Phosphorous acid has the formula H<sub>2</sub>PO<sub>2</sub>; its anhydrid is phosphorous oxid, P<sub>2</sub>O<sub>3</sub>. Pyrophosphoric acid, H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, metaphosphoric acid, HPO<sub>3</sub>, and hypophosphorous acid, H<sub>2</sub>PO<sub>2</sub>, are all known.

The acids of phosphorus are not used very extensively, but some of their salts are very important. Phosphoric acid forms three classes of salts, it being a tri-basic acid. To illustrate, tri-sodium phosphate, Na<sub>3</sub>PO<sub>4</sub>, di-sodium phosphate, HNa<sub>2</sub>PO<sub>4</sub>, and mono-sodium phosphate, H<sub>2</sub>NaPO<sub>4</sub>, are well-known salts of phosphoric acid. These phosphates and several of the hypophosphites are used quite extensively in medicines.

281. Phosphates as Fertilizers.—Plants and animals both need phosphorus, plants taking phosphorus from the soil, while animals are dependent upon plants for their supply. Most soils contain a greater or less supply of phosphorus in the form of phosphates. By continual cropping the soil may be deprived of its phosphorus just as we have seen that a soil may have its nitrogen compounds removed. For this reason practically all artificial fertilizers contain phosphates.

These phosphates may be obtained from guano, fish scrap, ground bone, or as is more often the case, from rock phosphates. The phosphate rock is treated with sulfuric acid to convert insoluble tri-calcium phosphate, Ca<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>, into an acid calcium phosphate, usually H<sub>4</sub>Ca(PO<sub>4</sub>)<sub>2</sub>, which is soluble and can be absorbed by plants. The reaction is as follows:

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow 2CaSO_4 + H_4Ca(PO_4)_2$$
.

This mono-calcium phosphate is often called super-phos-

phate of lime. The calcium sulfate formed is rather beneficial to plants.

Generally not enough sulfuric acid is used to convert all the tri-calcium phosphate into the super-phosphate and these two compounds then slowly interact to form reverted calcium phosphate, H<sub>2</sub>Ca<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>, a compound insoluble in water, but soluble in water containing carbon dioxid or in certain soil acids. This compound is not available for immediate use but it is slowly converted into a plant food.

The analysis of an artificial fertilizer should show not only the amount of phosphorus present equivalent to total phosphoric acid, but it should show what per cent. is equivalent to insoluble phosphoric acid, the per cent. equivalent to soluble phosphoric acid, and the per cent. equivalent to reverted phosphoric acid.

### ARSENIC

- 282. Occurrence.—Some arsenic is found uncombined in nature; it also occurs as the oxid, as sulfids, and in complex sulfids.
- 283. Preparation and Properties.—Most of the arsenic is obtained as a by-product from smelters. In roasting certain sulfid ores the arsenic they contain is oxidized and condenses in the flues of the smelter. It is removed and reduced with carbon to metallic arsenic.

Arsenic is a gray solid with a metallic luster. In its physical properties it resembles the metals, but chemically it behaves like the non-metal phosphorus, although it is less active. Heated in the air it unites with oxygen to form arsenious oxid, As<sub>2</sub>O<sub>3</sub>, commonly called white arsenic. Arsenic unites with nascent hydrogen to form arsine, H<sub>3</sub>As, a very poisonous gas with a garlic-like odor. Use is made of this reaction in Marsh's test for arsenic, an exceedingly delicate and reliable test for this element. It is especially important since practically all the compounds of arsenic are very poisonous.

284. Uses of Arsenic and Its Compounds.—The metal arsenic is used in hardening shot and in the manufacture of opal glass. White arsenic is used as an insecticide, especially by taxidermists. It also finds some use in medicine, and in the manufacture of certain pigments. Paris green is a compound containing arsenic and copper; it was at one time used quite extensively as a pigment. Its chief use now is as an insecticide.

Arsenic forms acids exactly analogous to those formed by phosphorus. Some arsenites and arsenates are quite important compounds, especially the arsenate of lead, Pb<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>, large amounts of this compound being used for spraying trees to destroy such noxious insects as the gypsy and brown-tail moths.

#### ANTIMONY

285. Occurrence and Properties.—Antimony occurs free in nature to some extent, but the sulfid, Sb<sub>2</sub>S<sub>3</sub>, commonly known as *stibnite*, is more abundant.

Antimony is a silver white element with a bright metallic luster; it is quite heavy and very brittle. It is less active chemically than arsenic, but when heated in the air it forms the trioxid, Sb<sub>2</sub>O<sub>3</sub>, a white volatile solid. With nascent hydrogen it forms *stibine*, H<sub>3</sub>Sb, a compound analogous to arsine. Antimony is not affected by hydrochloric acid, but it dissolves slowly in aqua regia forming a chlorid. Like arsenic, it forms a series of weak acids.

The hydroxid of this element is amphoteric, since under some circumstances it forms an acid and under other circumstances it forms a base. To illustrate, its hydroxid may ionize as in the following equations:

Thus we see that in the presence of a strong acid the hydroxid of antimony acts as a base, while it acts as a weak acid in the presence of a strong base like sodium hydroxid. Similar compounds of several elements show the same characteristics.

If we put antimony tri-chlorid in water, it not only hydrolyzes but dehydration occurs and a new type of compound is formed as represented by the equations:

$$\begin{array}{l} {\rm SbCl_3} + 2{\rm HOH} {\rightarrow} {\rm Sb(OH)_2Cl} + 2{\rm HCl} \\ {\rm Sb(OH)_2Cl} {\rightarrow} {\rm SbOCl} + {\rm H_2O}. \end{array}$$

At first a basic chlorid is formed, but it decomposes forming the *oxy-chlorid*, SbOCl, sometimes called the sub-chlorid.

286. Alloys.—By melting together two or more metals a substance, called an *alloy*, is often formed. In some cases an alloy appears to be merely a mixture of metals; in other cases a compound appears to be formed, since the proportion is definite. Some chemists now regard alloys as solid solutions of metals in one another.

An alloy may have properties quite unlike those of any of its constituents, or in some cases they may be intermediate. Usually the melting point of an alloy is lower than the average melting point of its constituents and often it is below that of any one of them.

287. Uses of Antimony.—Antimony is used in preparing several alloys. Type-metal contains antimony, lead, and tin; the antimony is especially important since it expands when it solidifies, and the type is thus made distinct and clear-cut. Antimony is also used in the non-friction alloy known as Babbitt's metal. Britannia metal, an alloy much used in making tableware, is an alloy of antimony, tin, copper, and often zinc.

The sulfids of antimony are used as pigments. They

also find use in vulcanizing rubber; red rubber contains antimony. Tartar emetic is a compound of antimony that is used quite extensively as a mordant in the dyeing of cotton goods.

#### BISMUTH

288. Bismuth.—Bismuth is a heavy metal that resembles antimony to considerable extent. It has a distinctly reddish hue. It is more metallic than antimony and forms bases more readily.

The chief use of bismuth is in the manufacture of the fusible alloys. Two common ones, Wood's metal and Rose's metal, melt at temperatures below that of boiling water. These fusible alloys are used as safety plugs in boilers, as fuses in electric wiring, in fire alarms and automatic sprinkling devices (see Fig. 82), and for automatically closing the doors of fireproof sa

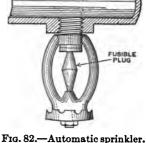


Fig. 82.—Automatic sprinkler.

closing the doors of fireproof safes.

Bismuth acts as a trivalent element in the formation of most of its compounds. It acts in the same manner as antimony when its salts are treated with water, hydrolysis first occurring and then dehydration. Thus the chlorid, BiCl<sub>3</sub>, forms an *oxy-chlorid* or *sub-chlorid*, BiOCl, when treated with water. The *sub-nitrate*, BiONO<sub>3</sub>, is used in medicine.

# SUMMARY

Of the allotropic forms of phosphorus, the yellow variety and the red are the most common. Yellow phosphorus is very active, even at the ordinary temperature. Red phosphorus is quite inert. Phosphorus is used as a poison, in making matches, and as a constituent of certain alloys.

The phosphates of calcium are important constituents of commercial fertilizers.

Arsenic is used for hardening shot; its compounds are used to some extent in medicines, for pigments, and as insecticides.

Antimony forms several alloys, the following being the most important: type-metal, Babbitt metal, and Britannia metal.

Bismuth is used in the manufacture of fusible alloys; its salts are used for medicine.

The following tabular form shows the rather close relationship between the elements of the nitrogen family.

	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic weights	14	31	. 75	120	208
Valence	3, 5 In oxids som	3, 5 e of the ele	3, 5 ments have	3, 5 a valence of	3, 5 1, 2, or 4
Hydrids	H <sub>2</sub> N	H <sub>2</sub> P	H <sub>2</sub> A <sub>8</sub>	H <sub>a</sub> Sb	
Oxids	N <sub>2</sub> O <sub>3</sub> N <sub>2</sub> O <sub>5</sub>	PrOs PrOs	A82O2 A82O4	Sb <sub>2</sub> O <sub>3</sub> Sb <sub>2</sub> O <sub>5</sub>	Bi <sub>2</sub> O <sub>2</sub> Bi <sub>2</sub> O <sub>5</sub>
Acids	HNO: HNO:	HaPOs HaPOs	HaAsOs HaAsO4	HaSbOa HaSbO4	
	Very strong acids	Weak acids	Weak acids	Very weak acids	Basic

#### **OUESTIONS AND PROBLEMS**

- 1. Why have laws been passed in many countries forbidding the use of yellow phosphorus for making matches?
- 2. If a solution of phosphorus in carbon disulfid is poured on a piece of filter paper, spontaneous combustion takes place as soon as the disulfid evaporates. Explain.

- 3. How does the strength of the acids in this family seem to depend upon the atomic weights? How does it appear to vary with the valence?
- 4. How could you prepare red phosphorus from the yellow? How could you prepare yellow phosphorus from the red?
  - 5. Complete the following structural formulas:

$$Na - O - H + H - O P = O \rightarrow H - O$$

$$Na - O - H + H - O P = O \rightarrow H - O$$

$$Na - O - H + H - O P = O \rightarrow H - O$$

$$Na - O - H + H - O P = O \rightarrow H - O$$

$$Na - O - H + H - O P = O \rightarrow H - O$$

$$Na - O - H + H - O P = O \rightarrow H - O$$

- 6. Why should the analysis of a fertilizer show the per cent. of each phosphate it contains as well as the total amount?
- 7. What per cent. of calcium phosphate, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, is phosphorus?
- 8. Under what circumstances does the hydroxid of antimony act as a base? When does it act like an acid?
- 9. How do you account for the fact that antimony and bismuth occur free in nature while phosphorus never does?
- 10. Write the formulas for three calcium phosphates. Write the formula for sodium arsenite.
- 11. Why is the use of arsenic as a pigment in wall papers forbidden?

#### CHAPTER XXVIII

# THE CARBON-SILICON GROUP

289. Carbon Group.—The two most important elements in this family are carbon and silicon. Their chemical properties are quite similar. Both have a valence of 4; their oxids and acids are analogous. While carbon is found free in nature to some extent, silicon is not found native.

#### SILICON

- 290. Occurrence.—Next to oxygen silicon is the most abundant element. A very large number of silicates are found, the majority of them being quite complex compounds. A very important compound of silicon is the dioxid, which is known as *silica*. Silicon monoxid is formed by heating sand with enough coke to remove half its oxygen. It is a yellowish-brown powder used as a paint.
- 291. Silica.—Silica has the formula SiO<sub>2</sub>, the compound being analogous to carbon dioxid. It is found in many different forms in nature.
- 1. Sand is the most common form of silica, and it is also one of the most useful. Large quantities of sand are used every year in the manufacture of glass. In several ways it is used as an abrasive. In the manufacture of sand-paper, a heavy paper is coated with glue and sand is then sprinkled over the surface. A sand-blast, which is used for polishing and cutting very hard surfaces, makes use of a stream of sand driven at a high velocity. Scouring soaps or powders usually contain powdered soap, washing soda,

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and powdered silica, the latter substance being "gritty" enough to do the scouring work. Sand is also used extensively in making mortar and concrete, while considerable quantities are used for lining molds, into which molten iron is to be poured for making castings. It is especially suitable for this purpose since it is infusible and quite easily removed from the casting after it has solidified.

- 2. Sandstone differs from sand only in that the particles are held together by a kind of cement. Sandstone is used as a building material; it is also sawed into slabs and used for sidewalks or for making grindstones.
- 3. Quartz is a transparent, crystalline variety of silica. Quartz crystals are six-sided prisms surmounted at each end by six-sided pyramids, each crystal having 18 faces (see plate of crystals). While pure rock crystal is colorless, traces of impurities impart to it characteristic colors. For example, amethyst, smoky quartz, rose quartz, and milky quartz are all well-known varieties of quartz.

Quartz is now melted and fashioned into tubing, crucibles, and other laboratory apparatus (see Fig. 83). Such apparatus is not as easily acted upon by acids and alkalis as ordinary glassware; it has so low a coefficient of expansion that it may be heated red hot and then plunged into cold water without breaking. Quartz is also drawn into very fine threads to be used as suspension fibers in very delicate electrical instruments.

- 4. Amorphous silica includes flint, jasper, chalcedony, sard, carnelian, onyx, and agate. The last two are made up of bands of different color. Fine specimens of both amorphous and crystalline silica are used as gems.
- 5. Silica in Plants and Animals.—Silica is found to considerable extent in plants, especially in the leaves and stems, where it appears to give rigidity.

Some one-celled marine animals have skeletons composed of silica, instead of the ordinary calcium compounds. These animals belong to the order infusoria; the diatoms are examples. Deposits of infusorial or diatomaceous earth, consisting of the microscopic remains of these animals, cover large areas of the ocean bottom as well as



Fig. 83.—Silica ware.

extensive land areas. We have already learned that dynamite consists of nitro-glycerin absorbed by infusorial earth. This form of silica is sold as a silver polish under the name *electro-silicon*.

292. Properties of Silica.—Pure silicon dioxid can be fused only at very high temperatures. It is insoluble in water and the common acids, with the exception of hydrofluoric acid, which acts upon it as follows:

$$\uparrow 
SiO2 + 2H2F2 \rightarrow SiF4 + 2H2O.$$

The silicon tetra-fluorid that is formed is volatile. Alkalis act upon silica more readily as a rule than the acids. 293. Silicic Acids.—Salts corresponding to several different silicic acids are found in nature. Since silicon has a valence of 4, it may form an acid having the formula H<sub>4</sub>SiO<sub>4</sub>. This orthosilicic acid forms, when partially dehydrated, meta-silicic acid. An acid formed by dehydrating another acid in the same series is always called a meta acid. Meta-silicic acid is analogous to carbonic acid; since it has the formula H<sub>2</sub>SiO<sub>3</sub>. Its relation to ortho-silicic acid is shown by the following equation:

$$\mathrm{H_4SiO_4} - \mathrm{H_2O} \rightarrow \mathrm{H_2SiO_3}$$
.

Silica appears to be the anhydrid of this acid, although the acid can not be formed by treating silica with water. The acids of silicon are *very* weak, unimportant compounds but some of their salts are very important.

294. Silicates.—The simplest silicates are those of sodium and potassium. Sodium silicate, Na<sub>2</sub>SiO<sub>3</sub>, is used as a filler of soaps, for fireproofing wood, and for making casts and artificial stone. Both sodium and potassium silicates are soluble, their solution being sold as water glass. When eggs are dipped in a solution of water glass, the pores of the shell are filled and decomposition does not readily occur. Thus water glass is used for preserving eggs.

Since theoretically di-silicic and tri-silicic acids may be formed by dehydrating two or three molecules of orthosilicic acid, silicates are usually quite complex. Furthermore, mixed silicates are formed, thus leading to still

greater complexity. Asbestos, mica, clay, granite, feldspar, garnets, and pumice stone are common examples of silicates.

295. Carborundum.—We have already learned that



Fig. 84.—Electric furnace for making carborundum.



Fig. 85.—Carborundum abrasives.

carborundum, or silicon carbid, is made by heating sand and coke in an electric furnace. Fig. 84 shows a commercial electric furnace used to make carborundum. This com-

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pound is a very hard substance and finds extensive use for grinding and polishing metals. It is made into hones, polishing wheels, and carborundum cloth. Fig. 85 shows specimens of carborundum and the finished wheels.

296. Glass.—Glass is a mixture of silicates. Ordinary glassware usually consists of the silicates of sodium and calcium. Potassium is sometimes substituted for sodium in some special kinds of glass, and lead or barium for calcium.

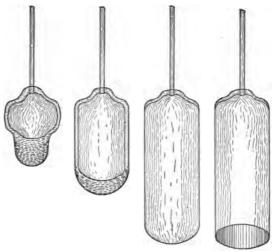


Fig. 86.—Diagrams of the various steps in blowing window glass.

In the making of ordinary glass a mixture of sand, sodium carbonate, and calcium carbonate is heated in a pot of fire-clay until fusion occurs. The heating is continued until all the gases are liberated, impurities being removed by skimming. Glass is suited to a wide variety of uses because of two characteristic properties. It is transparent, and it does not have a sharp melting point, but it gradually softens

or becomes plastic. Due to its plasticity, it may be rolled, blown, or pressed into practically any desired shape.

In making window glass the workman introduces into the furnace one end of a blowpipe about 6 ft. long and rolls it around until a sufficient amount of glass adheres to it (see Fig. 86). He then blows a large bubble in this glass and by

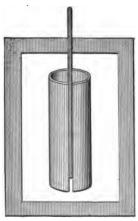


Fig. 87.—Flattening out a cylinder of window glass.

alternately swinging it and blowing it and then rolling it on a metal plate fashions it into a large cylin-The ends are then cut off, the cylinder is cut along one side and spread out flat (see Fig. 87). The various steps in blowing glass are also shown in Fig. 88. Bottles are blown in molds and then finished by using a special tool to shape the neck and round the edge (see Fig. 89). Plate glass is made by pouring the molten glass on a table and rolling it with a metal roller (see Fig. 90). It is then polished to make it highly trans-

parent. Cut glass is molded and a design is cut by means of a wheel. After that it is polished by the use of rouge, or iron oxid. Cheap glass dishes are sometimes made by pressing the glass into a mold to impart to the dish the desired design. Fig. 91 shows the method of drawing glass tubing and rodding.

When glass is cooled quickly it is very brittle, and liable to break very easily. To make glass less brittle it is annealed by cooling it slowly. This is accomplished by drawing the glass through a long oven, heated at one end and quite cool at the other. The process is a slow one, requiring in some cases several days.

Since sand usually contains some iron, ordinary glass is

slightly colored green by this impurity. If we look at the edge of a pane of window glass this color may be detected.



Fig. 88.—Various steps in glass blowing.

While this color does not interfere in any way with window glass, yet glass to be used for lenses in optical instruments

must be free from such coloration. The green color is neutralized by the addition of manganese dioxid, the product being known as *crown glass*. When potassium is substituted for the sodium in making glass, the product is



Fig. 89.—Lamp bowl blown in mold.

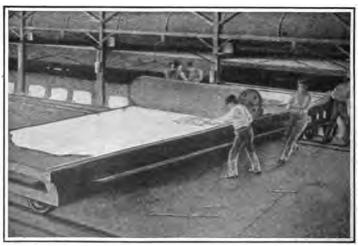


Fig. 90.—Rolling plate glass. (Permission of Scientific American.)

much harder and less easily melted. The hard glass, or Bohemian glass that is used for certain laboratory purposes is a potassium glass. It is also less readily acted upon by alkalis than sodium glass; hence it is sometimes known as



Fig. 91.—Drawing thermometer tubing.

"resistance" glass. Flint glass contains lead; it is a soft, lustrous, heavy glass. Its index of refraction is considerably higher than that of ordinary glass, hence it refracts light more readily, giving a better play of colors. It is used in making cut glass and to some extent for making imitation gems.

Glass is colored by the addition of various substances to the molten mass. The addition of iron compounds produces a dirty bottle green. If more manganese dioxid is added than the amount required to neutralize the iron in making crown glass, an amethyst color is produced. Cobalt gives a blue color while calcium fluorid makes it white and translucent.

#### SUMMARY

The most important elements in the carbon family are carbon and silicon.

Silica has the formula SiO<sub>2</sub>; it occurs in nature as sand, sandstone, the several varieties of quartz, amorphous varieties such as flint, agate, and onyx, and to some extent in plants and animals.

Glass is a mixture of silicates. The raw materials used in making glass are sand, sodium carbonate or sulfate, calcium carbonate, potassium carbonate, and lead oxid.

Flint glass, crown glass, and Bohemian glass are the chief varieties. Glass is colored by the addition of metallic oxids to the fused mass.

Silicates are salts of silicic acid. Talc, mica, asbestos, granite, feldspar, and pumice stone are common silicates found in nature.

Carborundum is a carbid of silicon. It is used as an abrasive.

# QUESTIONS AND PROBLEMS

- 1. Summarize the uses of silicon dioxid.
- 2. Why is it so difficult to remove the stoppers from ground-glass bottles that are used to contain sodium hydroxid? Would this

difficulty also occur if the bottle were used as a container for sodium carbonate solution? Explain.

- 3. How do you account for the small seams seen along the sides of cheap bottles?
  - 4. What are the advantages of "resistance" glass?
- 5. Write equations to show how complex silicic acids may be formed by dehydrating two molecules of ortho-silicic acid. By dehydrating three molecules of ortho-silicic acid.
- 6. Why is sand the final product formed by the disintegration of the majority of igneous rocks?
- 7. Glass fruit-jars generally have a greenish tint. Is this color an advantage or a disadvantage?
- 8. Would it be desirable to have milk bottles that have a decided greenish tint? Give a reason for your answer.
- 9. Tell how ordinary window glass is made. Describe the process of annealing and tell why it is so important.
- 10. Give the composition of flint glass. What are its properties?
- 11. How does ordinary glass differ from hard glass in composition?
- 12. Why should aqua ammonia not be used for washing cut glass?

Topics for Reference.—Wire glass. Prism glass and its uses.

# CHAPTER XXIX

# OCCURRENCE OF METALS AND METHODS OF EXTRACTION

- 297. Metals.—The elements studied thus far have been largely acid-forming elements. They are the non-metals. Of the elements that remain to be studied, all with the exception of boron have base-forming properties. They are called metals. It is of interest to inquire how these elements are found in nature. Instead of taking up the occurrence of each metal in detail, thus involving a great deal of pure memory work, an attempt will be made in this chapter to so outline this subject that it may be well covered in a more general way. This plan depends upon a study of the activity of the metals, and of the stability and insolubility of their compounds.
- 298. Metals Occurring Free.—Such metals as gold and platinum are very inactive, not uniting readily with other elements; thus they are generally found *free* in nature. Other metals sometimes occurring free are silver and copper.
- 299. Solubility of Oxids.—The oxids of sodium, potassium, calcium, barium, and strontium are either soluble in water or they act chemically with water. Thus we should hardly expect to find these oxids in nature. Such is the case. On the other hand, the oxygen of the air is so widely distributed, and it is such an active element, that the insoluble oxids of the other metals form some of the most important compounds in nature.
- 300. Sulfids.—The sulfids are analogous to the oxids with respect to insolubility, and metallic sulfids are even

more widely distributed than the oxids. For example, sulfids of lead, zinc, copper, silver, iron, and mercury are quite abundant.

- 301. Hydroxids.—With the exception of the hydroxids of sodium, potassium, calcium, barium, and strontium, metallic hydroxids are *insoluble*. They do not occur so abundantly as the sulfids and oxids of the metals, since they are less stable, either losing water to form an oxid, or uniting with carbon dioxid to form a carbonate.
- 302. Carbonates.—The carbonates of sodium and potassium are soluble. Other carbonates are insoluble, hence many carbonates are found in nature
- 303. Sulfates.—In a study of the compounds that are to follow the work will be shortened if a list of the *insoluble* compounds is given. Of the sulfates, those of barium, strontium, and lead are *insoluble*; the sulfates of silver and calcium are only *slightly soluble*. Other sulfates are quite readily soluble. As might be expected, the sulfates of barium, calcium, strontium, and lead all occur in nature.
- 304. Chlorids.—The chlorids of lead, silver, and mercurous mercury are *insoluble*; other metallic chlorids are *soluble*. Contrary to what might be expected, the chlorids of sodium, potassium, and magnesium are quite abundant. Since they are all very soluble, their occurrence appears to be due to some extent to their high heat of formation and consequent relative stability; it is also true that all the ordinary compounds of sodium and potassium are also soluble.
- **305.** Nitrates.—All nitrates are soluble. Nitrate of sodium is the only nitrate that occurs at all extensively in natural deposits; it is found in desert regions.
- 306. Conclusions.—To summarize, we may expect: (1) to find inactive metals occurring uncombined; (2) to find such natural compounds as the sulfids, oxids, and carbonates of the heavy metals (this conclusion naturally follows

a consideration of Berthollet's law of insolubility); (3) to find only those soluble compounds that are very stable, or the compounds of elements all of whose compounds are soluble.

#### METALLURGY

307. Metallurgy Defined.—Metallurgy is the science that deals with the extraction of metals from their ores. A study of the metallurgy of each element involves a great deal of memory work, since the details of the method used depend upon the expense of the operation, the properties of the metal, and the nature of the ore that is being used. Let us first distinguish between mineral and ore as used in metallurgy. A mineral is an element or compound occurring naturally as the result of some organic or inorganic process. An ore is a mineral that contains an element in such quantity and form that it may be profitably extracted. For example, clay is an aluminum mineral; it is not an aluminum ore, since the expense of extracting aluminum from clay makes the cost prohibitive.

In this chapter, we shall aim to describe and illustrate four general methods of extracting metals from their ores. While a few metals are not extracted by any one of these processes, yet one of them, or a modification of it, is employed in a great majority of cases.

308. Electrolysis.—We have had several examples illustrating the fact that compounds can be decomposed by passing an electric current through their solutions. Electrolysis is used quite extensively for extracting metals, but since many ores are not water soluble, and the dry ore is a non-conductor of electricity, the *fused ore* is generally used. For example, in preparing sodium, the sodium chlorid to be electrolyzed is fused. If a solution of sodium chlorid were used in this case, the sodium would attack the water to form sodium hydroxid as fast as the electroly-

sis took place. The same is true of potassium, calcium, and to some extent magnesium.

Electrolysis is a practical method of extracting metals when the metal is a very active one, and a cheap source of power for generating electricity is available. In this country electrical industries flourish at Niagara Falls, making use of the enormous hydro-electric power there developed. At present the cost is greater than that of extracting metals by other methods; for that reason electrolysis is limited mainly to the extraction of very active metals. Since aluminum is used more extensively than any other metal prepared by electrolysis, we will illustrate the general method by describing the electrolysis of bauxite, an aluminum ore.

309. Extraction of Aluminum by Electrolysis.—The method used at present for extracting aluminum was worked

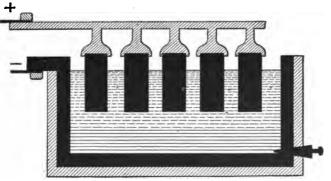


Fig. 92.—Electrolysis of aluminum oxid.

out by Charles M. Hall. Bauxite is a hydrated oxid of aluminum, but it is infusible. Hall learned that it dissolves readily in cryolite, a fusible mineral that comes from Greenland.

An iron box lined with carbon is made the cathode, while rows of carbon rods are used as the anode. The box is

kept heated above the melting point of both cryolite and aluminum. When the current is passed through such a solution of bauxite in cryolite, electrolysis occurs; the aluminum sinks to the bottom of the box and is drawn off

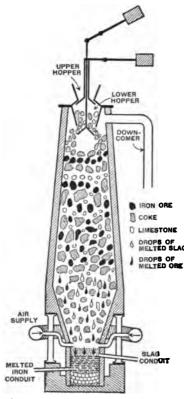


Fig. 93.—Diagram of blast furnace.

from time to time. The oxygen is liberated at the anode. Fresh bauxite is added periodically so that the action may be continuous (see Fig. 92).

310. Reduction with Carbon.—The reduction of oxids of metals with carbon forms the most important method used in metallurgy. Sulfids and carbonates of metals are subjected to a preliminary treatment known as roasting before they are heated with car-Thus these comhon. pounds are converted into  $\mathbf{b}\mathbf{v}$ heating them oxids while exposed to air.

The reducing agent generally used is coke, since it is not only very efficient, but it is also moderately cheap. Charcoal was at one time extensively used and coal is occasionally

used at the present time. In 1915 the United States alone produced more than 30,000,000 tons of iron. When we consider that about 1 lb. of coke is needed for the extraction of 1 lb. of iron, we can form some estimate of the

enormous quantities of coke that are used annually, not only in the iron and steel industry, but also for the reduction of copper, tin, and zinc. The process of extracting metals by reduction may be illustrated by describing somewhat in detail the operation of a blast furnace in the preparation of iron.

311. Use of a Blast Furnace for Reducing Iron.—The furnace used in this operation consists of a steel shell from 80 to 100 ft. high, and from 20 to 25 ft. internal diameter, lined with fire-brick (see Fig. 93). Water circulates through a shell built in the walls at the part where the greatest heat is produced to protect this portion. The heat is due to chemical action which is started by forcing a blast of hot air into the furnace through tuyères. Hence the name blast furnace. Fig. 94 shows a blast furnace with the "stoves" that are used for heating the air for the blast.

The charge consists of iron ore, coke, and a flux. Limestone is used as the flux when the ore contains silica as an impurity. If the ore already contains limestone, then sand is used as a flux.

The chemical action is quite complex. Oxidation of the coke first occurs resulting in the formation of carbon dioxid. As this gas comes into contact with the layers of coke above, it is reduced to carbon monoxid,

$$CO_2 + C \rightarrow 2CO$$
,

which interacts with the iron ore as follows:

$$Fe_2O_3 + 3CO \rightleftharpoons 3CO_2 + 2Fe$$
.

Since the reaction is reversible, it may be driven to the right only when there is a decided excess of carbon monoxid. For this reason the waste gases contain about 20 to 30 per cent. of carbon monoxid which is removed at the top of the

furnace and conducted away to be used as fuel. The iron sinks to the bottom of the furnace where it is drawn off every 4 to 6 hours. When it solidifies in molds it forms pig iron.



Fig. 94.—A blast furnace for reducing iron ores. The "stoves" seen at either side heat the air for the blast.

The flux serves three purposes: (1) It unites chemically with the impurities to form a slag which is removed from the furnace by tapping at intervals of about 2 hours. (2)

The slag that is formed has a lower melting point than the impurities in the ore hence less heat is required. The word flux comes from the word fluere (to flow), and it is used in chemistry to designate any substance that lowers the melting point of a mixture to which it is added thus rendering it more fluid. (3) Since the slag is fairly light it covers the surface of the iron and protects it from subsequent oxidation that might occur from the air blast.

A blast furnace is kept in continual operation, a double trap being so arranged at the top that the charge may be added without disturbing the action or without loss of gas. Its life is in some cases as high as 20 years and some of the large ones have a capacity of from 600 to 900 tons a day.

312. Alumino-thermics.—When raised to a temperature high enough to start the reaction, aluminum combines with oxygen and enormous quantities of heat are liberated. In fact the heat of formation of aluminum oxid is so great that granular aluminum readily takes oxygen from the oxids of other metals, leaving them uncombined.

Aluminothermy is practical in metallurgy under certain conditions. (1) When small quantities of a carbon-free metal are required. (2) It is used to extract metals not easily reduced by carbon, provided the metals are more valuable than aluminum itself. At the present time, chromium, which is used quite extensively in making some special steels, is extracted by heating its oxid with aluminum. Manganese is another metal that is extracted by the same method. Some non-metals, such as silicon and boron, may be reduced with metallic aluminum. (3) While aluminothermy can not be used on a large scale for preparing iron, since the cost is too great, yet some iron is liberated in this manner to be used for autogenous welding. The process was worked out by Dr. Hans Goldschmidt. A mixture of

granular aluminum and iron oxid, known as thermit, is placed in a crucible over the metals to be welded. An igniting mixture, consisting of barium peroxid and powdered aluminum or magnesium, is placed on top of the thermit to start the reaction (see Fig. 95). The chemical action is as follows:

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$
.

As the white hot molten iron is reduced it runs down over the broken ends and literally fuses them together to form a



Fig. 95.—Thermit crucible as used for welding.

solid piece (see Fig. 96). The temperature produced by the reaction is estimated at more than 3000°C.

313. Replacement.—If we suspend a strip of copper in a

solution of silver nitrate, the copper gradually goes into solution and metallic silver is precipitated.

$$Cu + 2AgNO_3 \rightarrow Cu (NO_3)_2 + 2Ag.$$

Use is sometimes made of this fact in metallurgy, cheap metals being used to prepare more expensive ones. For example, iron will precipitate from solution such metals as copper, silver, and gold. In the following paragraph a replacement table is given from which it is possible to determine not only the order of replacement, but also several other interesting facts concerning metals.



Fig 96.—The completed weld made by the use of thermit as in Fig. 95.

314. Replacement Series.—The position of any metal in the adjoining table depends upon its relative tendency to ionize. Potassium enters the ionic condition more readily than other metals; for that reason it stands first in the replacement series. Since potassium ionizes more readily than iron, it will replace iron from solutions of iron compounds. For the same reason iron replaces copper, silver, or gold. In short, an element will replace any element that stands below it in the replacement series; it will be replaced from its compounds by any element standing above it in the table.

## REPLACEMENT SERIES

· Potassium Sodium Barium Strontium Calcium Magnesium Aluminum Manganese Zinc Chromium Iron Cobalt Nickel Tin Lead HYDROGEN Copper Mercury Silver

Platinum

Gold

The farther apart any two elements stand in the series, the greater the potential difference produced by those two metals when used make a voltaic cell. For that reason this series is sometimes called the  $T_{\Lambda}$ electromotive series. illustrate, copper and zinc may produce an electromotive force of 1.1 volts: copper and iron give only 0.67 volt: but silver and aluminum furnish more than volts.

The elements that stand above hydrogen in the series are not found free in nature, while those below hydro-

gen are frequently found uncombined. Hydrogen chlorid does not act on any of the metals below hydrogen, since these metals do not replace hydrogen from its compounds. The metals below hydrogen may be acted upon by such strong oxidizing acids as nitric and sulfuric, but hydrogen is not liberated. An oxid is first formed which is then converted into a salt of the acid and water by the subsequent action of the acid.

The metals that stand above zinc can not be reduced by hydrogen alone. Those that stand above manganese are prepared by electrolysis. They are the most active metals, being readily acted upon by acids, water, and oxygen, with the exception of aluminum. The metals that fall below copper do not tarnish in air. Their oxids are easily decomposed by heating. Since water contains some hydrogen ions, most of the metals that stand above hydrogen in the series interact with water, or *rust* when exposed to moisture.

## SUMMARY

All oxids, sulfids, and hydroxids are insoluble except those of sodium, potassium, calcium, barium, and strontium, and of these the oxids and sulfids generally unite chemically with water.

All ordinary carbonates are insoluble except the carbonates of sodium and potassium.

The minerals and ores found most abundantly in nature are oxids, sulfids, and carbonates.

The sulfates of barium, strontium, and lead are insoluble; the sulfates of silver and calcium are slightly soluble; all other sulfates are soluble.

The chlorids of lead, silver, and mercurous mercury are insoluble; other chlorids are soluble.

All nitrates are soluble.

Metallurgy is the science that deals with the extraction of metals from their ores.

With few exceptions, metals are extracted by one of the following methods: electrolysis; reduction; aluminothermy; replacement. The light metals are generally extracted by electrolysis. The common heavy metals are extracted by reducing their ores with carbon. Metals less widely used and the more valuable metals are extracted by aluminothermy or by replacement with a cheaper metal.

# QUESTIONS AND PROBLEMS

- 1. The only soluble silicates are those of sodium and potassium. Would you expect to find silicates widely distributed in nature?
- 2. Why are the metals that stand above hydrogen not found free in nature?

- 3. From the position of mercury in the replacement series, what do you think would be the effect of heating cinnabar, or mercuric sulfid?
- 4. Which metal do you think would be more easily reduced, iron or copper? Iron or aluminum?
- 5. Why is it necessary to fuse the ore before extracting metals by electrolysis?
  - 6. Distinguish between metal, mineral, and ore.
- 7. State the advantages and disadvantages of extracting metals by electrolysis.
- 8. What is the chief objection to the use of aluminothermy in metallurgy?
- 9. What is meant by the term "flux" as used in metallurgy? State its uses in extracting iron?
- 10. Summarize the facts that may be observed by a careful study of the replacement series of metals.

Reference Topic.—The value of Hall's discovery to metallurgy.

# CHAPTER XXX

# ALKALI METALS

315. The Sodium Family.—Sodium and potassium are the most important metals of this family. They were discovered by Sir Humphrey Davy early in the nineteenth century. The hypothetical metal ammonium is similar in its chemical properties to these metals and belongs in this group. Sodium and potassium are often called alkali metals since their hydroxids are very strongly alkaline. The valence of all the elements in this group is one, as is also the valence of the ammonium radical. All ordinary compounds of these metals are soluble in water. Sodium and potassium occur in nature as chlorids, the former being very widely distributed. Potassium chlorid and also the sulfate are found in quantities at Stassfurt, Germany, associated with compounds of calcium and magnesium. The Stassfurt deposits occur in beds several hundred feet thick. The metals in this group are all prepared by electrolysis.

### SODIUM

316. Properties of the Metal.—Sodium is a silver white metal, so light that it floats on water. It is so soft that it may be molded like wax. Chemically it is one of the most active metals. It unites with oxygen so readily that it must be kept in oil to prevent oxidation. It also unites chemically with most non-metals; it interacts with water and with all ordinary acids. Sodium forms some of the most important chemical compounds known to chemistry.

The metal finds some use as a reducing agent. Used as a catalytic agent it converts isoprene, a hydrocarbon having the formula C<sub>5</sub>H<sub>8</sub>, into artificial rubber.

317. Sodium Chlorid.—NaCl. Sodium chlorid, or common table salt, occurs in nature in sea-water, in salt-wells, and in rock deposits. Rock-salt is mined in some localities, but most of the salt of commerce is obtained by the evaporation of natural brines, either by the use of natural or artificial heat. In this country, New York, Michigan, Ohio,



Fig. 97.—Harvesting salt from San Francisco Bay. (Permission of Scientific American.)

Kansas, and a few other States are large salt-producers. The United States produces more than 30,000,000 barrels annually. Sodium chlorid crystallizes in cubes. Pure salt is not deliquescent, but magnesium chlorid, a very deliquescent compound, is usually present as an impurity. This accounts for the fact that salt becomes wet and "packs" in moist weather (Fig. 97).

Sodium chlorid, as the cheapest compound of sodium, is used as a starting point in the manufacture of all sodium compounds and also of all compounds containing chlorin.

Thousands of tons of salt are used every year as a preservative, in packing and curing meats. Mixed with snow and ice, salt forms a good freezing mixture. It is estimated that the average American uses about 11 lb. of salt a year in seasoning his food. Considerable quantities are fed to sheep and cattle.

- 318. Sodium Nitrate.—NaNO<sub>3</sub>. Extensive beds of sodium nitrate are found in Western South America, especially in the desert regions of Northern Chile. It is a colorless, crystalline compound, slightly hygroscopic. Large quantities of sodium nitrate are used for fertilizers. Since it is the only nitrate found to any considerable extent in nature, it is used for making nitric acid and other nitrates. Since it absorbs water, it is not suitable for making gun-powder.
- 319. Sodium Sulfate.—Na<sub>2</sub>SO<sub>4</sub>. Sodium sulfate, a byproduct from the manufacture of hydrochloric acid, is used in making glass and sodium carbonate. It forms colorless crystals, having the formula Na<sub>2</sub>SO<sub>4</sub> · 10H<sub>2</sub>O, used in medicine under the name Glauber's salt.
- 320. Sodium Hydroxid.—NaOH. In the chapter on bases we learned that sodium interacts with water to form sodium hydroxid. This compound is produced commercially by the electrolysis of a solution of sodium chlorid, the electrodes being in separate compartments so that the chlorin which is liberated at the anode does not by any chance come into contact with the hydrogen or the sodium hydroxid formed at the cathode. Sodium hydroxid is a white, crystalline solid. In purified form it is often cast in sticks. It is deliquescent, taking on first water from the air and then carbon dioxid, changing slowly into the carbonate. In water solution it forms one of the strongest known bases. Since it attacks the flesh and skin it is known as caustic soda. Its most important use is in making soap. For household use, such as cleaning sinks, it is known as lue.

321. Carbonates of Sodium.—Na<sub>2</sub>CO<sub>3</sub>. HNaCO<sub>3</sub>. Two carbonates of sodium are very important, the carbonate and the bi-carbonate. In the United States they are made by the Solvay process, while in France the LeBlanc process is still largely used.

Solvay Process.—In this process a saturated solution of sodium chlorid is treated with ammonia and carbon dioxid. The ammonia dissolves in the water and combines with the carbon dioxid to form ammonium bi-carbonate:

$$H_3N + H_2O + CO_2 \rightarrow H_4NHCO_3.$$
 (1)

The sodium chlorid interacts with the ammonium bicarbonate to form sodium bi-carbonate:

$$NaCl + H_4NHCO_3 \rightarrow H_4NCl + HNaCO_3.$$
 (2)

If the carbonate is desired it may be obtained by heating the bi-carbonate:

$$\begin{array}{c}
\uparrow \\
2\text{HNaCO}_3 \rightarrow \text{Na2CO}_3 + \text{H2O} + \text{CO}_2.
\end{array}$$
(3)

The Solvay process is a very interesting one, as it shows clearly how by-products may be utilized. The process was devised by Ernest Solvay, a Belgian. In a large plant at Solvay, N. Y., the raw materials used are salt, limestone, and coal. The Solvay Company operates its own gas plant. From this plant gas and coke are obtained, both being used for fuel and power. The ammonia which enters into the manufacture of the soda is a by-product of this gas plant. The carbon dioxid used is obtained by heating limestone, and quick-lime is produced at the same time:

$$\begin{array}{c}
\uparrow \\
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2.
\end{array}$$

This quick-lime is slaked,  $CaO + H_2O \rightarrow Ca(OH)_2$ , and heated with the ammonium chlorid obtained from the gas plant as in equation (2):

All the products are either used over again in the process or put on the market as by-products except the calcium chlorid which remains after the recovery of the ammonia. No important use has yet been found for this crude chlorid.

LeBlanc Process.—This process is an older one than the Solvay and it is more expensive. Some valuable byproducts are obtained, hence the process is still largely used. Sodium chlorid is treated with sulfuric acid to form sodium sulfate and hydrochloric acid:

$$2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}. \qquad (a)$$

The sodium sulfate is then reduced to sodium sulfid by heating it with carbon:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2.$$
 (b)

When sodium sulfid is heated with calcium carbonate, sodium carbonate and calcium sulfid are produced:

$$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS.$$
 (c)

The calcium sulfid is converted into sulfur and bleaching powder, which form valuable by-products. The most important by-product, however, is the hydrochloric acid prepared as shown in equation (a).

Sodium carbonate forms colorless crystals having the formula Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O. It is used extensively in the manufacture of glass. It hydrolyzes to some extent in water forming a basic solution. For this reason it is used in laundries under the name of washing soda. This carbonate is also used to soften hard waters.

Sodium bi-carbonate is generally known as baking soda. It interacts with acids or acid salts liberating carbon dioxid which we have learned is a leavening agent. With the

lactic acid in sour milk it interacts to form sodium lactate, water, and carbon dioxid:

In order that baking soda may be used as a leavening agent with water or sweet milk, it is mixed with starch and some acid or a salt and sold as baking powder. There are three well-known classes: cream of tartar powders, acid phosphate powders, and alum powders.

With cream of tartar powders the action is as follows. Rochelle salts being produced and carbon dioxid set free:

$$(CHOH)_{2} \underbrace{\begin{array}{c} COOH \\ COOK \\ Acid potassium tartrate \end{array}}_{Acid potassium tartrate} + \underbrace{\begin{array}{c} Na - O \\ H - O \\ Sodium bicarbonate \\ (CHOH)_{2} \\ COOK \\ COOK \\ Sodium potassium tartrate \\ (Rochelle salts) \end{array}}_{COOK} + \underbrace{\begin{array}{c} 1 \\ H_{2}O + CO_{2}. \end{array}}_{COOK}$$

In the phosphate powders calcium acid phosphate is used.

$$\begin{array}{c} \operatorname{CaH_4(PO_4)_2} + \operatorname{2HNaCO_3} \to \operatorname{CaHPO_4} + \operatorname{Na_2HPO_4} + \\ \operatorname{Mono-calcium}_{\text{phosphate}} & \operatorname{Sodium}_{\text{bi-carbonate}} & \operatorname{Calicium acid}_{\text{phosphate}} & \operatorname{Di-sodium}_{\text{phosphate}} \\ & \uparrow \\ 2\operatorname{H_2O} + \operatorname{CO_2}. \end{array}$$

Alum is not an acid salt but it hydrolyzes in water and acts like an acid

Considerable discussion has arisen as to the healthfulness of powders containing alum. It is quite evident that alum itself interferes with digestion. It has also been claimed that the aluminum hydroxid which is formed is injurious, but unfortunately sufficient work has not been done to establish the truth or falsity of this belief. Most of the investigations along this line have been carried out by rival manufacturing companies; thus they are less apt to be free from bias. At the present time alum is used in several brands of baking powder. Starch is added to baking powder to keep it dry. Not more than 20 per cent. is necessary for this purpose, but sometimes as high as 50 per cent. may be added by the manufacturer.

322. Sodium Peroxid.—Na<sub>2</sub>O<sub>2</sub>. When sodium is burned in the air a yellowish-white powder is formed; it is peroxid of sodium. This peroxid unites with water to form sodium hydroxid while oxygen is set free.

$$Na_2O_2 + H_2O \rightarrow 2NaOH + (O)$$

Since nascent oxygen is liberated in this reaction such a solution forms an excellent bleaching agent. Because fibers bleach more readily in an alkaline solution, sodium peroxid is taking the place of hydrogen peroxid to a considerable degree as a bleaching agent. To be used for preparing oxygen, sodium peroxid is sold under the name oxone.

- 323. SodiumThiosulfate.—Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. This compound is commonly called "hypo." It is used in photography as a fixer to dissolve the unchanged silver salt that has not been reduced by the action of the light and the developer. It is also used as an "antichlor."
- 324. Sulfites of Sodium.—Na<sub>2</sub>SO<sub>3</sub>. HNaSO<sub>3</sub>. These sulfites are used in the bleaching industry and as preservatives. The acid sulfite, HNaSO<sub>3</sub> is used in the paper industry.
- 325. Di-sodium Phosphate.—HNa<sub>2</sub>PO<sub>4</sub>. Although three phosphates of sodium are known, the di-sodium phosphate is the most important. It is used in medicine.

### POTASSIUM

- 326. Metallic Potassium.—In its physical properties potassium resembles sodium very closely. It differs in color, having a slight blue tinge. It is more active chemically than sodium.
- 327. Potassium Hydroxid.—KOH. The method of making potassium hydroxid is analogous to that of preparing sodium hydroxid. It resembles the hydroxid of sodium in both physical and chemical properties. In fact they are so much alike that usually one may be substituted for the other. Since the hydroxid of sodium is much cheaper, potassium hydroxid is not very extensively used.
- 328. Potassium Chlorid.—KCl. The chief source of potassium chlorid is the deposit at Strassfurt, Germany. It is a white, crystalline solid. With potassium sulfate, K<sub>2</sub>SO<sub>4</sub>, which is also found in the Stassfurt deposits, it furnishes the "potash" used for fertilizers. It is the starting point for potassium compounds.
- 329. Potassium Carbonate.—K<sub>2</sub>CO<sub>3</sub>. Potassium carbonate is present in wood ashes. Wool perspiration, or suint, also contains potassium carbonate which is now recovered from the waters used in washing wool. Considerable potassium carbonate is present in the mother liquor left after sugar crystals have been obtained from sugar beets. These illustrations show the important relation of potassium compounds to plant and animal life. The most important use for potassium carbonate is in the manufacture of hard glass.
- 330. Potassium Nitrate.—KNO<sub>3</sub>. This compound is made by mixing hot concentrated solutions of sodium nitrate and potassium chlorid. We would expect the action to be reversible,

$$KCl + NaNO_3 \rightarrow KNO_3 + NaCl$$
,

but sodium chlorid, being less soluble than the other com-

pounds in hot water, separates first as crystals. Potassium nitrate when mixed with sulfur and powdered charcoal forms black gun-powder. It is also used to some extent for curing meats, especially corned beef. Chopped meats retain their bright red color when sprinkled over with a little potassium nitrate.

331. Potassium Chlorate.—KClO<sub>3</sub>. When the halogens are introduced into a solution of an alkaline hydroxid two reactions may occur. If the solution of the hydroxid is cold and dilute, a reaction like the following occurs:

$$2KOH + Cl_2 \rightarrow KCl + KClO + H_2O.$$

Both the hypochlorite and the chlorid of potassium are formed. If the solution of the hydroxid is hot and concentrated an entirely different reaction takes place:

$$6KOH + 3Cl_2 \rightarrow 5KCl + KClO_2 + 3H_2O$$
.

The latter reaction is made use of in the manufacture of chlorates. Potassium chlorate is a white crystalline solid. It is a very vigorous oxidizing agent, hence it finds considerable use in the manufacture of matches, explosives, and fireworks. Chlorate of potash tablets are used for sore throat.

332. Other Potassium Compounds.—Both potassium bromid, KBr, and potassium iodid, KI, are used in medicine and in photography. Potassium acid carbonate, KHCO<sub>3</sub>, was formerly used for baking under the name saleratus.

#### AMMONIUM COMPOUNDS

333. Ammonium Chlorid.—H<sub>4</sub>NCl. Ammonia and hydrogen chlorid combine to form ammonium chlorid, a white crystalline salt. The reaction is reversible, depending upon the temperature:

$$H_4NCl \rightleftharpoons H_2N + HCl.$$

- It is often called sal ammoniac; it is used in voltaic cells, for soldering, and to some extent, in medicine.
- 334. Ammonium Sulfate.— $(H_4N)_2SO_4$ . This compound is obtained as a by-product in the manufacture of coal gas. It is a very valuable fertilizer.
- 335. Ammonium Nitrate.—H<sub>4</sub>NNO<sub>3</sub>. We have already learned that this compound is used to prepare nitrous oxid, or laughing gas. It is also used to prepare "safety explosives" for use in mines. Marsh gas, which is often liberated in coal mines, forms an explosive mixture with air. Most explosives used for blasting will ignite this mixture of marsh gas and air, but ammonium nitrate mixed with rosin or sulfur forms an explosive which does not usually generate enough heat when it explodes to ignite the marsh-gas mixture.
- 336. Ammonium Sulfid.— $(H_4N)_2S$ . Ammonium sulfid is a liquid prepared by passing hydrogen sulfid into ammonium hydroxid. It is used as a reagent in qualitative analysis.
- 337. Ammonium Carbonate.—(H<sub>4</sub>N)<sub>2</sub>CO<sub>3</sub>. This white solid slowly decomposes giving the acid carbonate and ammonia. It is used as a laboratory reagent, for smelling salts, and in making aromatic spirits of ammonia.
- 338. Flame Tests.—Several metals when heated high enough to be volatile burn with a characteristic flame. This furnishes an excellent means of identifying them. The test is made as follows: A platinum wire is held in the flame until it is clean or until it imparts no color to the flame. It is then dipped into the salt or solution to be identified and again held in the flame. Sodium imparts an intense yellow color to the flame; the potassium flame is violet; lithium and its compounds give a crimson flame; barium compounds give a yellowish-green flame. Unfortunately this simple test is often obscured by the presence of other compounds; a spectroscope is then necessary to distinguish one element from others that may also be present.

## SUMMARY

The alkali metals are prepared by the electrolysis of their fused chlorids. Their hydroxids are prepared by the electrolysis of solutions of their chlorids. These hydroxids are very strong bases.

The chlorids of sodium and potassium occur in nature. They are used in preparing other sodium and potassium compounds. Potassium chlorid is an important fertilizer.

Sodium nitrate is used as a fertilizer; it is also used for making nitric acid and in the preparation of potassium nitrate which is used in the manufacture of black gunpowder.

The carbonates of both sodium and potassium are used in the glass industry. Sodium carbonate is known as washing soda; sodium bi-carbonate is used as baking soda, and as an essential constituent in baking powders.

Sodium peroxid is an important oxidizing agent used in the bleaching industry.

Potassium chlorate is made by passing chlorin into a hot concentrated solution of potassium hydroxid. It is used as an oxidizing agent in matches, fireworks, and explosives.

Ammonium salts are similar in many respects to the salts of sodium and potassium. The chlorid, sulfid, sulfate, and nitrate are the most important salts. Ammonium hydroxid is an active base although much weaker than sodium or potassium hydroxid.

Some metals impart to a flame a characteristic color by which they can be identified. Sodium gives an intense yellow flame; potassium, a violet flame.

# QUESTIONS AND PROBLEMS

- 1. Why is sodium chlorid so important commercially?
- 2. How many grams of hydrochloric acid can be neutralized by 10 grams of sodium hydroxid? How many grams of the same acid would 10 grams of potassium hydroxid neutralize?

- 3. Crystallized sodium carbonate, Na<sub>2</sub>CO<sub>3</sub> · 10H<sub>2</sub>O, effloresces when exposed to the air and forms Na<sub>2</sub>CO<sub>3</sub> · H<sub>2</sub>O, a white powder. Would it be cheaper to buy the former at 10 cents per pound or the latter at 15 cents per pound? In each case find the cost of 1 lb. of anhydrous sodium carbonate.
- 4. Why are water solutions of sodium carbonate and sodium bicarbonate alkaline? Which would you expect to be more strongly alkaline?
- 5. How many pounds of potassium nitrate can be made from 100 lbs. of sodium nitrate and 100 lbs. of potassium chlorid?
- 6. How could you distinguish potassium nitrate from sodium nitrate? How could you distinguish potassium chlorid from the nitrate?
- 7. How many pounds of nitric acid can be made from 300 lbs. of sodium nitrate that is 87 per cent. pure?
- 8. If sold at the same price per pound, which would be cheaper to use as a leavening agent, sodium bi-carbonate or potassium bi-carbonate?
- 9. In what laboratory experiments have the following compounds been used: sodium chlorid; sodium ritrate; potassium chlorate; sodium carbonate; ammonium chlorid; ammonium nitrate?
- 10. How many pounds of sodium hydroxid may be made from 1 ton of salt?

Reference Topics.—Stassfurt mineral deposits. History of the LeBlanc process. Use of the spectroscope.

# CHAPTER XXXI

# ALKALINE EARTH GROUP

339. General Family Characteristics.—This family consists of three elements: calcium, barium, and strontium. Like the alkali metals these elements may be prepared by electrolysis, but since they have little practical application, the demand is small. They interact with water but not so rapidly as the alkali metals. Their hydroxids form strong bases, hence this family is sometimes called the "alkaline earth group." Calcium, barium, and strontium have a valence of 2. They are never found free in nature.

## CALCIUM

340. Calcium Carbonate.—CaCO<sub>3</sub>. One of the most abundant compounds of calcium is the carbonate. It is also one of the most useful.

Limestone is one of the important forms. Although pure calcium carbonate is white in color or colorless when crystalline, the natural deposits are usually colored by the presence of organic matter or iron compounds. It is used as building stone, especially for foundation work. Enormous quantities are heated to produce quick-lime. With or without cement crushed limestone is extensively used for making and repairing roads. Tons of limestone are used every year as a flux in the reduction of metals, especially iron. We have already learned that it is used in the making of soda, glass, and carbon dioxid.

Calcite is a crystalline variety of calcium carbonate.

Transparent colorless specimens are known as *Iceland spar*. They exhibit the property of double refraction of light.

Marble consists of fine grains of calcite. By subjection to natural heat and pressure, limestone is changed into marble. Since it takes a high polish and is easy to cut, marble is used for statuary, monuments, and as a finishing stone.

The shells of such animals as clams, snails, and oysters consist largely of calcium carbonate. In past ages, shell

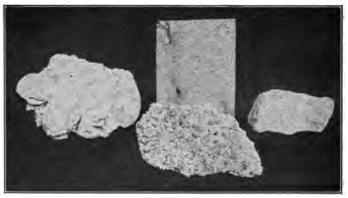


Fig. 98.—Varieties of calcium carbonate, including a slab of polished marble, fossil-bearing limestone (left), oölite (right), and coquina (center).

deposits from such animals became firmly cemented together forming large masses of solid rock. Old Fort Marion, at St. Augustine, Florida, is built of a shell rock called *coquina* (see Fig. 98). *Chalk* is of geologic formation, consisting of the microscopic remains of small marine animals.

Precipitated chalk is an artificial calcium carbonate prepared by the action of calcium chlorid on sodium carbonate.

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl.$$

It is soft and finely divided, forming a non-gritty scouring powder, suitable for tooth powders.

341. Caves.—Limestone caves occur in the earth's crust due to the solubility of calcium carbonate in a water solution of carbon dioxid. The carbonate, while insoluble in water, dissolves readily in carbonic acid forming the bi-carbonate:

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons H_2Ca(CO_3)_2$$
.

The bi-carbonate is carried away in solution by the underground waters leaving large caverns. If the crust above falls into the cavern, it forms what is called a *limestone* sink. The above reaction is reversible. As the water



Fig. 99.—Stalactites and stalagmites in Marengo cave. (Salisbury's Physiography, by permission.)

solution of calcium bi-carbonate drops from the roof of the cave, some evaporation occurs and carbon dioxid is liberated. Thus the insoluble calcium carbonate which is thrown out of solution hangs from the roof in icicle-like masses called *stalactites*. Upon the floor of the cave further precipitation occurs forming *stalagmites* (see Fig. 99).

342. Calcium Oxid.—CaO. Calcium oxid, or quick-lime,

is made by heating limestone in large furnaces called *lime-kilns*.

$$\begin{array}{c}
 \uparrow \\
 \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2.
 \end{array}$$

Pure calcium oxid is a soft, white, amorphous compound. It is very refractory, melting or vaporizing only at the temperature of the electric arc. It unites chemically with water to form calcium hydroxid.

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 + 15,540$$
 calories.

During this union with water a marked expansion occurs and large quantities of heat are evolved. When lime is exposed to the air, moisture and carbon dioxid unite with it slowly producing air-slaked lime. It consists of both the hydroxid and the carbonate, and is not so suitable for use in making mortar as quick-lime.

343. Calcium Hydroxid.—Ca(OH)<sub>2</sub>. Calcium hydroxid, which we have seen is made by slaking calcium oxid, is a white solid, only slightly soluble in water. Its water solution, known as lime-water, is a strong base. Since calcium hydroxid is the cheapest base, it finds extensive application, being used to remove hair from hides, in liming soils, in the manufacture of ammonia, glass, and bleaching powder, and in softening hard water. A suspension of calcium hydroxid in water, called milk of lime, is used for whitewash.

One of the most important uses of lime is in the preparation of mortar. *Mortar* consists of a mixture of freshly slaked lime and sand. During the hardening or "setting" of mortar, water is first lost by evaporation. Then carbon dioxid is *slowly* taken up from the air, especially at the surface, resulting in the formation of calcium carbonate and the liberation of water:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O.$$

Thus the soft calcium hydroxid gradually changes into a hard stony mass; the sand makes the mortar porous, giving a more free circulation of air to facilitate hardening; it also prevents undue contraction and increases the hardness and strength of the mass. When mortar is to be used as plaster, hair is generally added to make it more tenacious until hardening can occur.

344. Cement.—Cements are classified as natural cements, and artificial or Portland cements. Some limestone rocks contain clay in the proper proportion to form a natural

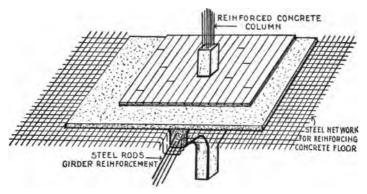


Fig. 100.-Methods of reinforcing concrete.

cement when heated to a very high temperature. Natural cements set rather quickly but are not so strong as some of the artificial cements. Portland cement is made by heating an artificial mixture of limestone and clay and then grinding the product to a very fine powder.

The hardening of cements is not well understood; it appears to be due to the union of its components with water to form hydrates. Since they have the property of hardening under water, they are called hydraulic cements.

Concrete is made by mixing together cement, water, sand, and crushed stone. Upon "setting" it forms a very hard

compact mass. Thus it is used for making building blocks, sidewalks, bridges, foundations, floors, and the walls of dams. Reinforced concrete is concrete that is strengthened

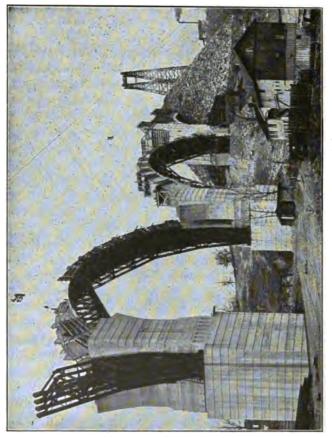
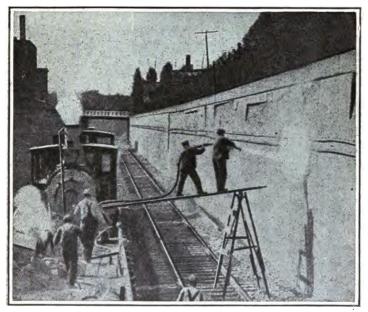


Fig. 101a.—Reinforced concrete viaduct.

by imbedding in it rods of iron or steel (see Fig. 100). It is used extensively in structural work (see Fig. 101, a and b). In 1915 the United States produced more than 87,000,000

barrels of cement, more than 10 times the quantity produced in 1900. So rapid has been the increase in production and so varied are the applications of cement that the present age may with considerable justice be called the cement age (see Fig. 102).



Frg. 101b.—Concrete atomizer in operation. (Permission of Scientific American.)

345. Calcium Sulfate.—CaSO<sub>4</sub>. Calcium sulfate occurs in nature as the mineral *gypsum*. Transparent crystals of gypsum are known as selenite. A white opaque variety, known as *alabaster*, is used for statuary. Since it is soft enough to be easily scratched with the thumbnail, it is one of the easiest minerals to carve.

When gypsum is heated to a temperature of 110° to 130°C., it loses part of its water of crystallization and forms

a white substance known as plaster of Paris. When this plaster is mixed with water it sets rapidly, taking on water

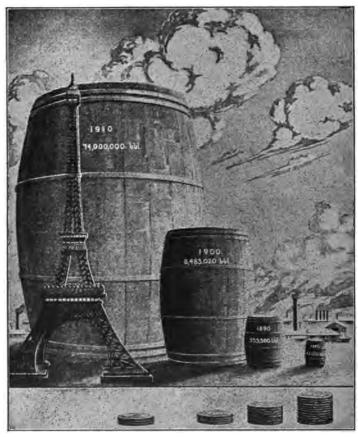


Fig. 102.—Relative increase in the amount of cement used from 1880 to 1910, and the corresponding decrease in price. (Permission of Scientific American.)

of crystallization again, and forming a hard white substance. Plaster of Paris finds use in making casts, in plastering when a very white coating is desired, and in making stucco, which also contains glue and stone.

Gypsum is also used as a fertilizer, for calcimining, and as a filler for paper and paints.

346. Other Calcium Compounds.—We have already studied calcium chlorid, CaCl<sub>2</sub>, used as a drying agent; the calcium phosphates, used in fertilizers; calcium cyanamid, CaCN<sub>2</sub>, also used as a fertilizer; and calcium carbid, CaC<sub>2</sub>, used for making acetylene.

# BARIUM AND STRONTIUM

347. Strontium and Barium are found in nature as sulfates and carbonates. Barium sulfate, BaSO<sub>4</sub>, is used as a filler for making heavy paper, as a pigment, and as an adulterant of white paint. Barium compounds give a yellowish-green flame. They are used for making fireworks. Barium peroxid, BaO<sub>2</sub>, is a strong oxidizing agent; it is used in the manufacture of hydrogen peroxid.

Strontium compounds burn with a bright red flame. Strontium nitrate,  $Sr(NO_3)_2$ , is used as red fire in pyrotechnics. Strontium hydroxid,  $Sr(OH)_2$ , unites with sugar to form an insoluble sucrate. It is used in the beet-sugar industry to remove the last traces of sugar from the "mother liquor." The sucrate is then decomposed with carbon dioxid to recover the sugar.

## SUMMARY

The carbonates and sulfates of calcium, barium, and strontium are important compounds found in nature.

Calcium carbonate is used as limestone for building purposes, as a flux, in making glass, and in the manufacture of quick-lime.

Quick-lime, or calcium oxid, is a white, soft solid that unites with water to form the base calcium hydroxid.

When a cheap base is needed for industrial operations, calcium hydroxid is generally used. For softening water, for removing the hair from hides, for making ammonia and bleaching powder, and in the preparation of mortar, calcium hydroxid is used extensively.

Mortar is a mixture of slaked lime, sand, and water. Plaster usually contains the foregoing constituents and hair.

Cement is prepared by heating a mixture of calcium carbonate and clay and then reducing the product to a very fine powder. With sand, crushed stone, and water, it forms concrete, a substance largely used for building materials. Concrete may be reinforced by having imbedded in it bars of iron or steel.

Calcium sulfate is used as a fertilizer and in the manufacture of plaster of Paris.

Barium and strontium compounds are used in the manufacture of fireworks.

# QUESTIONS AND PROBLEMS

- 1. How many pounds of calcium oxid may be obtained from 1 ton of limestone? How many pounds of slaked lime will it make?
- 2. What action might result if calcium oxid were placed in leaky freight cars for shipment?
- 3. Why do the walls of newly plastered houses remain damp for so long a time?
- 4. Bottles containing lime-water often become covered with a white coating that is not easily washed off. How can it be removed chemically?
  - 5. Why is air-slaked lime not desirable for making mortar?
- 6. What action occurs when marble is strongly heated? Write the equation.
- 7. Why does a wood fire aid in a new house in hardening the plaster?
- 8. Why does blowing air or steam into a lime-kiln hasten the production of lime?

- 9. Would limestone be completely converted into lime and carbon dioxid by heating it in a closed tube? Explain.
- 10. Compare the "setting" of mortar, plaster of Paris, and cement.
- 11. Starting with calcium carbonate, write all the equations representing the chemical preparation of calcium oxid, calcium hydroxid, calcium chlorid. How much hydrochloric acid would be required if you used 250 grams of calcium carbonate, 90 per cent. pure?
- 12. Could barium hydroxid be substituted for calcium hydroxid as a base?
- 13. How could the flame test be used to identify barium and strontium?

Topics for Reference.—Famous limestone caves. The use of concrete in building the Panama Canal. Florida East Coast. Railway extension to Key West.

## CHAPTER XXXII

## THE MAGNESIUM FAMILY

348. The Family.—The magnesium family consists of four elements: magnesium, zinc, cadmium, and mercury. The resemblance that is so marked in the families already studied is not so close in this group of elements. The properties vary from magnesium, which is quite an active metal, to mercury, an inactive metal. The valence of the group is 2, although mercury sometimes has a valence of 1.

#### MAGNESIUM

- 349. Magnesium is a silver-white metal, having a specific weight of 1.75. It is not acted upon by dry air but in moist air a coating of basic carbonate forms on its surface. This layer protects the metal underneath. It decomposes hot water slowly with the liberation of hydrogen. All common acids interact vigorously with magnesium. In air magnesium burns readily, producing a very white light rich in actinic rays. The metal is put on the market in ribbon form, wire form, or as a fine powder. It finds use in making flashlight powders and in fireworks. Magnesium forms an alloy with aluminum known as magnalium. This alloy is light and tenacious; it is being used in the construction of airplanes and automobiles.
- 350. Magnesium Compounds.—Magnesium compounds resemble the compounds of calcium quite closely. *Magnesium oxid*, MgO, is a very refractory compound used for lining crucibles, furnaces, and for making fire-brick. With

ZINC 301

magnesium chlorid the oxid forms a basic salt that is used as a cement for artificial stone floors. Magnesium sulfate, MgSO<sub>4</sub>, is used in medicine under the name Epsom salts. The silicates of magnesium include such well-known compounds as talc, or soap-stone, asbestos, and meerschaum. Soap-stone is used for table-tops and sinks. When powdered it is known as talcum powder or French chalk. Asbestos is a fibrous mineral that is manufactured into a fire-proof paper or cloth. Meerschaum is used for pipe-bowls, cigar-holders, etc.

### ZINC

- 351. Zinc.—The most important ore of zinc is the sulfid, from which the metal is extracted by reduction with carbon. Zinc is a bluish-white metal. At the ordinary temperature it is somewhat brittle but at a slightly increased temperature it becomes malleable and ductile. Rolled or drawn zinc does not become brittle upon cooling. Zinc burns with a bluish-white flame forming zinc oxid. Dry air does not affect zinc, but moist air acts upon it forming a basic carbonate. The tarnish thus formed adheres to the surface of the zinc and protects the metal underneath. A metal that forms such an adherent, impervious coating upon exposure to the air is said to be self-protective. The ordinary acids act upon zinc.
- 352. Uses of Zinc.—Large quantities of zinc are used in making galvanized iron. The iron is thoroughly cleaned and then dipped into molten zinc. The zinc that adheres to the surface of the iron prevents the rusting of the iron. In some cases galvanizing is done by plating the iron with zinc. Occupying the position it does in the electromotive series, zinc is a suitable element for use as the negative plate of voltaic cells.

Zinc forms some very useful alloys. Brass is an alloy consisting of zinc and copper. Bronze contains copper,

tin, and usually zinc. German silver contains copper, zinc, and nickel.

353. Compounds of Zinc.—All soluble zinc compounds are poisonous. Zinc oxid, ZnO, is a white solid used as a paint base under the name zinc white. It does not have so great a covering power as white lead, and it tends to scale off, but it has the advantage of lead in that it does not turn black when exposed to gas fumes or air containing hydrogen sulfid. Zinc sulfate, ZnSO<sub>4</sub>, is a white crystalline solid. It is used as a battery fluid, and to some extent as a fungicide and insecticide. Zinc chlorid, ZnCl<sub>2</sub>, is used to prevent the decay of wood that is to be used in contact with the earth, such as railroad ties, posts, etc. Creosote is largely surpassing zinc chlorid for this purpose at present.

## CADMIUM

**354.** Cadmium is usually found associated with zinc. It resembles zinc and magnesium in the nature of its compounds. Cadmium is used in some of the fusible alloys. Cadmium sulfid is a yellow compound used as an artist's color.

## MERCURY

355. Properties.—The quicksilver mines of Spain are the richest in the world. Some quicksilver is produced in California. Mercury, or quicksilver, is a heavy silver-white metal with a metallic luster. It is the only metal that is a liquid at the ordinary temperature. It freezes at -39°C. and boils at 357°C. Its specific weight, 13.6, is higher than that of the common metals. Thus iron, zinc, copper, tin, and lead float on mercury.

Mercury does not tarnish when exposed to the air. When heated in the air it slowly changes into a red powder, mercuric oxid, HgO. Since mercury stands below hydrogen

in the replacement series, it can not replace that element from hydrochloric acid. Such strong acids as nitric and sulfuric act upon it, nitric acid very vigorously. Hydrogen is not liberated in such cases, but it unites with a part of the oxygen of the acid to form water, and such reduction compounds as nitric oxid, nitrogen peroxid, or sulfur dioxid are set free respectively.

356. Uses.—The following properties of mercury make it suitable for use in thermometers: (1) It has quite a low freezing point and a high boiling point; (2) it has a much higher coefficient of expansion than glass; (3) its expansion is uniform, especially between 0°C. and 100°C. To illustrate, a column of mercury increases the same amount when heated from 20° to 21°C. that it does when heated from 40° to 41°C. Mercury is suitable for use in barometers since it has so high a specific weight. Mercury is a fairly good conductor of electricity; it is convenient for such use when a good contact is desired. Mercury finds some use in the collection of soluble gases and in certain kinds of air-pumps. Mercury forms alloys with many other metals known as amalgams. In extracting gold and silver the powdered mineral containing these precious metals is treated with

amalgams. In extracting gold and silver the powdered mineral containing these precious metals is treated with mercury to form amalgams from which the gold and silver may be recovered by distilling the mercury. Tin amalgam is used for the backs of cheap mirrors. An amalgam consisting largely of silver, tin, and mercury is used for filling teeth. The zincs used in voltaic cells are amalgamated with mercury to prevent local action between the zinc and its impurities. Amalgams appear to be solutions of metals in mercury, or in some cases definite compounds.

357. Compounds of Mercury.—Mercury forms two classes of compounds: mercurous, in which the valence is 1; and mercuric, in which the valence is 2. Mercurous chlorid, Hg<sub>2</sub>Cl<sub>2</sub>, is a white solid, quite insoluble in water. It is used in medicine as a liver stimulant under the name

calomel. Mercuric chlorid, HgCl<sub>2</sub>, is a white crystalline solid moderately soluble in water. It is also known as the bi-chlorid of mercury and as corrosive sublimate. It is a deadly poison, as are all soluble compounds of mercury. The best antidote for mercury poisoning is the whites of raw eggs, or milk may be used. The mercury forms an insoluble compound with the albumin of the eggs or milk. Mercuric chlorid is used as an antiseptic for sterilizing surgical instruments. Mercuric sulfid, HgS, is a black solid when precipitated from mercury solutions. When sublimed it forms a red solid used as the pigment known as vermilion.

## SUMMARY

Magnesium is an active silver-white metal. It burns with a very intense white light. It finds use in flashlight powders, fireworks, and in the alloy magnalium. The oxid, sulfate, and several natural silicates are the most important compounds of magnesium.

Zinc is bluish-white. It is self-protective, hence it forms a good coating for the protection of iron. It interacts with acids forming salts of which the sulfate and chlorid are the most important. Zinc oxid is a very important compound finding use as a paint base. Brass, bronze, and German silver are alloys containing zinc.

Mercury is the only metal that is liquid at the ordinary temperature. It is quite inactive, air or hydrochloric acid having no effect upon it. It dissolves in nitric acid and hot concentrated sulfuric. Mercury finds considerable use in the manufacture of scientific instruments. Its alloys are called amalgams.

Mercuric sulfid is a red pigment known as vermilion. Two chlorids are important: mercurous chlorid, or calomel, is used as medicine; mercuric chlorid, or corrosive sublimate, is used as an antiseptic.

# **OUESTIONS AND PROBLEMS**

- 1. How much magnesium chlorid must be electrolyzed to give 100 lb. of magnesium?
- 2. Flashlight powders contain powdered magnesium and potassium chlorate. Account for their explosive nature.
- 3. How did you find the equivalent weight of magnesium in the laboratory?
- 4. Write the equation to show the chemical action that occurs when a strip of zinc is immersed in a solution of copper nitrate.
- 5. Why is zinc oxid superior to white lead as a paint base when used for interiors?
- 6. Would you expect a solution of zinc chlorid to give an acid or an alkaline reaction?
- 7. A sample of sphalerite, ZnS, is 70 per cent. pure. How many pounds of zinc can be obtained from 1 ton of this ore? How many pounds of zinc white, or zinc oxid, will it make?
  - 8. Name three methods used to prevent the decay of wood.
- 9. Cinnabar, the chief ore of mercury, has the formula HgS. What per cent. of cinnabar is mercury? How many pounds of calomel can be made from 100 lb. of the ore, if it is 90 per cent. pure?
- 10. What properties of mercury make it suitable for use in thermometers? For use in barometers?
- 11. What compound do you think would be formed by heating a mixture of mercuric chlorid and mercury?

# CHAPTER XXXIII

# THE ALUMINUM FAMILY

358. The Group.—Of several elements in this group, boron and aluminum are the only ones that are of sufficient importance to be discussed in an elementary text. The similarity between boron and aluminum is not well-marked. Boron is really an acid-forming element, in many ways resembling silicon. Elements in this group have a valence of 3.

## BORON

359. Boron.—As an element boron has no practical value. Two of its compounds have considerable importance, boric acid and borax. Boric acid, H<sub>3</sub>BO<sub>3</sub>, crystallizes in white lustrous scales. It occurs in nature in volcanic regions, especially in Tuscany, where it issues from the earth in steam-jets. Boric acid is a weak acid; its vapor imparts a green color to the flame. It has antiseptic properties, and is used as an eye-wash and mouth-wash. It is sometimes used as a preservative. The borates of some metals, especially tin borate, are used for making enamels.

In the United States borax, or sodium tetra-borate, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, is found in California and Nevada. It is used as a mordant, for softening hard water, and as an antiseptic and preservative. Since it dissolves metallic oxids, it is used in soldering and welding to give a clean surface.

## ALUMINUM

360. Properties.—Aluminum is a white metal whose specific weight is only 2.6; it is only one-third as heavy as 306

iron. It is both malleable and ductile, but not so tenacious as brass, copper, or steel. Aluminum is a good conductor of heat and electricity, being surpassed in this respect by silver, copper, and gold only. It may be welded or cast, but it can be soldered only with difficulty.

Although aluminum takes a high polish, it soon becomes dull as a result of the formation of a very thin coating of the oxid. This gives the metal a slight bluish tint. It is a self-protective metal. Hydrochloric acid acts readily on aluminum. Nitric acid hardly affects it at all Hot, concentrated sulfuric acid dissolves aluminum forming the sulfate. Salt water corrodes aluminum rapidly and the alkalis interact with it readily.

361. Uses.—To some extent aluminum is taking the place of copper as an electrical conductor, since a larger wire may be used with less strain on the support. As a purifier, aluminum is used to combine with gases that tend to make steel porous. The use of aluminum in thermit and in the extraction of metals has already been studied. Powdered aluminum is used as a protective paint, as in the "silvering" of radiators. When quite pure, aluminum makes excellent cooking utensils, since it is light, a good conductor of heat, and not easily tarnished. Its salts are not poisonous.

Aluminum bronze is an alloy of aluminum and copper. It is hard, elastic, of a golden color, and takes a high polish. When a smaller percentage of copper is used, aluminum bronze resembles silver. Magnalium is an alloy of aluminum and magnesium.

362. Aluminum Oxid.—Al<sub>2</sub>O<sub>3</sub>. Corundum and emery are natural oxids of aluminum. Rubies and sapphires are pure specimens of aluminum oxid colored by the presence of traces of metallic oxids. Synthetic rubies and sapphires are now made from molten aluminum oxid. The white sapphire consists of the pure oxid. Blue sapphires are

colored by titanium oxid, rubies by chromium. These artificial gems are identical in color and properties with the natural stones and can not be distinguished from them. *Emery* is used as an abrasive in the form of emery paper, cloth, or as grinding wheels. *Alundum* is an artificial oxid of aluminum made by fusing bauxite in an electric furnace. It is used for making crucibles for laboratory use and as an abrasive (see Fig. 103).



Fig. 103.—Alundum, a much used abrasive.

363. Aluminum Hydroxid.—Al(OH)<sub>3</sub>. When sodium hydroxid is added to a solution of an aluminum salt, a white, gelatinous precipitate of aluminum hydroxid is formed:

$$AlCl_3 + 3NaOH \rightarrow 3NaCl + Al(OH)_3.$$

This precipitate is insoluble in water but it dissolves, forming sodium aluminate, if we add the sodium hydroxid in excess.

$$Al(OH)_3 + 3NaOH \rightarrow Na_3AlO_3 + 3H_2O.$$

This reaction shows the amphoteric nature of aluminum

hydroxid. In the presence of a strong acid it ionizes to form a very feeble base:

$$Al(OH)_3 \rightarrow Al^{+++} + 3(OH^-)$$

When treated with a strong base like sodium or potassium hydroxid it ionizes as a very weak acid:

$$Al(OH)_3 \rightarrow 3(H^+) + AlQ_3$$
.

Aluminum hydroxid is such a weak base that its salts with weak acids are almost completely hydrolyzed. We would *expect* to have aluminum carbonate precipitated if we add sodium carbonate to a solution of aluminum chlorid:

$$2AlCl_3 + 3Na_2CO_3 \rightarrow 6NaCl + Al_2(CO_3)_3$$

Such is not the case.

If any aluminum carbonate is formed it instantly hydrolyzes to form the hydroxid:

$$Al_2(CO_3)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2CO_3.$$

Aluminum hydroxid is also precipitated when sodium sulfid is added to the solution of an aluminum salt.

Aluminum hydroxid is used in the coagulum method of purifying water and as a mordant in dyeing cotton and linen fabrics. Aluminum hydroxid unites with many dyes to form an insoluble compound known as a lake. Many dyes do not adhere directly to cotton and linen but such a gelatinous substance as aluminum hydroxid readily sticks to the fibers. When the fibers have been impregnated with such a compound, usually by hydrolysis, and then dipped in the dye bath, the dye unites with the mordant to precipitate a lake on the fibers. Thus the mordant fixes the dye so it does not wash out. Lakes of different colors may be produced with the same dye by varying the mordant. Lakes are often used as pigments.

364. Dyeing.—Formerly the chief source of dyes was from animal, plant, and mineral compounds. In 1856 Perkin succeeded in preparing mauve artificially from a coal-tar product by oxidizing aniline. Now a great many dyes are made synthetically from coal-tar, a substance that before the above date was considered almost worthless.

A good dye should have a pleasing shade; it should not fade when exposed to the light; it should not be removed from the fabric by rubbing, washing, or perspiration; it should not weaken the fiber. Wool and silk are sometimes dyed directly, as these fibers combine with certain dyes without the use of a mordant.

Some insoluble dyes such as indigo are precipitated on the fiber. Indigo is now prepared artificially. In the presence of a reducing agent it forms indigo white, a compound soluble in alkalis. When textile fibers are saturated with a solution of indigo white and then exposed to the air, oxidation occurs, resulting in the formation of the insoluble indigo blue. This dye is extensively used in dyeing blue serge. The color is very fast.

Acid dyes, which consist of alkali or calcium salts of color acids, are used in acid solution. They are not used for dyeing cotton and linen, but they dye silk and wool directly. Acid dyes are very fast to light, but they can not be washed with a soap or powder containing any free alkali, since a base causes the acid dye to dissolve rapidly.

On the other hand, basic dyes fade quite rapidly when exposed to the light, but they are not removed by washing. They dye wool and silk directly, but when used with cotton or linen, a mordant is required. Such dyes as methyl violet, methylene blue, malachite green, fuchsine, etc., are examples of basic dyes.

To secure good results in dyeing, the fabric must be thoroughly cleansed; it should be wet when introduced into the dye bath; the dye should be kept slowly boiling; and the goods should be agitated so all parts will be dyed uniformly. In dyeing cotton goods, the addition of such salts as sodium chlorid or sodium sulfate makes the dye less soluble and causes more of it to unite with the fabric.

365. Alums.—If we mix solutions of potassium sulfate and aluminum sulfate and then evaporate the mixture, a double salt separates as crystals. The formula of this alum is  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ . Any double sulfate formed in the same manner and having similar properties is called an alum. Instead of potassium sulfate, either sodium or ammonium sulfate is often used. Such trivalent metals as iron and chromium may take the place of the aluminum. The general formula,  $M'_2 M'''_2 (SO_4)_4 \cdot 24H_2O$ , is used to represent alums, in which M' is some univalent element, or group, and M''' a trivalent metal. Alums are used as mordants.

366. Silicates of Aluminum.—Fuller's earth is a silicate of aluminum used for cleaning fabrics and for clarifying oils. Ordinary mica is a potassium aluminum silicate. It is translucent and infusible. Under the incorrect name of isinglass it is used in stoves. As an insulator mica is used in making commutators for dynamos and motors. feldspars are complex silicates, usually containing aluminum silicate with either sodium or potassium silicate. By the action of water and carbon dioxid, disintegration or weathering occurs and the alkalis are leached out as soluble silicates or carbonates leaving a white clay, or hydrated aluminum silicate, known as kaolin. The colored clays found in soils usually contain iron and sometimes calcium. the color being largely due to iron compounds. Ultramarine is a complex substance made by heating together clay, soda, and sulfur. It is found in nature as the mineral lapis lazuli. The artificial product is a more highly colored pigment; it is used also as a laundry blue, and to neutralize the yellow tint of sugar, wood pulp, and linen fibers.



Fig. 104.—Kilns in which the famous Satsuma pottery is fired. (Copyright by Keystone View Company.)

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367. Applications of Clays.—Clay becomes plastic when it is mixed with water and it can be molded into any desired shape. When this plastic mass is dried and baked at a high temperature it does not melt but it contracts and forms a hard porous mass capable of resisting pressure. This property of clay makes it suitable for use in making brick, earthenware, and porcelain. In making bricks an impure clay is used. The red color is due to the presence of iron compounds. In making vitrified brick a high enough temperature is used to start fusion, thus filling the pores at the surface. Fire-bricks are made of clay and sand. Earthenware and tile are made from coarse clavs and a low temperature is used in "firing," so the mass remains porous. Flower-pots are examples of this ware. When such clays are heated to a higher temperature they are vitrified throughout the mass forming stoneware. The cheaper kinds of stoneware are glazed by throwing salt into the furnace. Porcelain or china is made from a very pure white clay mixed with powdered feldspar. It is usually fired twice. After the first firing the porous biscuit is dipped into water containing in suspension a mixture of powdered feldspar and kaolin. During the second firing the feldspar melts and fills the pores so that the china becomes impervious to liquids (Fig. 104).

## SUMMARY

Boric acid and boron are the most important compounds of boron. Both find some use as antiseptics and preservatives. Borax is used in soldering and welding to dissolve the tarnish and give a clean surface.

Aluminum is a light, white metal. It is a good conductor of heat and electricity. It is self-protective. Aluminum is used for paint, to purify steel, for electrical conductors, and in making cooking utensils.

Natural and synthetic rubies and sapphires consist of

aluminum oxid. Impure aluminum oxid is used as an abrasive.

Aluminum hydroxid may act as a base or an acid. It is used in purifying water and as a mordant.

Alums are double sulfates that find some use as mordants.

Mica, clay, and fuller's earth are silicates of aluminum. Clay is used in making bricks, earthenware, stoneware, and porcelain.

# QUESTIONS AND PROBLEMS

- 1. What precautions should be taken in using aluminum cooking utensils?
- 2. What advantages has aluminum when used for cooking utensils?
  - 3. What are the purposes of a mordant? What is a lake?
- 4. What elements have we studied that act as either acid formers or base formers? In what groups in the periodic table are these elements found?
- 5. Why is aluminum hydroxid precipitated when a solution of sodium carbonate is added to the solution of an aluminum salt?
- 6. Write the equations to show what action occurs when sodium sulfid is added to a solution of aluminum chlorid.
- 7. Aluminum acetate is the aluminum salt of a weak acid. What reaction do you think would occur if a piece of cloth were soaked in aluminum acetate and then treated with steam?
- 8. Why should alkaline scouring powders not be used for washing aluminum ware?
- 9. Should aluminum ware be polished frequently? Give a reason for your answer.
- 10. How many pounds of aluminum would be required to reduce the iron in 20 lb. of iron oxid by the thermit process, if the oxid has the formula  $Fe_2O_3$ ?

Topics for Reference.—Decorating pottery. The manufacture of enamels.

# CHAPTER XXXIV

# SOILS

368. Bed-rock, the Source of Soils.—The bulk of the earth's crust is made up of solid rock, or what is commonly called bed-rock. When such agents as oxygen, carbon dioxid, water, and other substances, act upon bed-rock, they convert it into mantle rock or soil. The process by which bed-rock is converted into mantle rock is known as weathering. Plants and animals, wind, and alternate freezing and thawing also aid in breaking large masses of rock up into smaller fragments.

Soils formed by weathering may remain just where they were formed, or they may be transported to another locality. In the first case they form residual soil. Wind, running water, and glaciers are the most important agents engaged in transporting soil. Much of the deep, fertile soil of the Middle West was brought down from Canada by prehistoric glaciers. Running water often carries the most fertile part of one farm down stream to some other farm where it is deposited, or it may be carried into the ocean and lost as farm soil. The depth of the soil varies from a few feet in some places to scores of feet in others.

369. Kinds of Soil.—The nature of a soil depends upon the constituents of the rock from which it was formed. When sandstone weathers a sandy soil is formed; the disintegration of limestone forms a limy soil; clay soils are formed by the weathering of shale, slate, feldspar, and granite. Granite is a mixed rock; when the quartz it contains weathers sand is the product formed; when the

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mica and feldspar weather, clay is produced. 'A transported soil is quite apt to be a mixed soil since the transporting agent may bring the materials of which it is composed from different sources. A mixture of sand and clay is called loam. If the amount of clay is relatively large, it is called a clay loam; if it is small in proportion to the amount of sand, the soil is a sandy loam. The decomposition of organic matter in the soil forms humus. When the decay of organic matter is quite rapid, on account of its being exposed first to the air and then to water, muck is formed. It is soft and spongy, and has usually lost all resemblance to the organic matter from which it was formed.

370. Elements Needed by Plants.—The elements absolutely needed by plants include carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, sulfur, calcium, iron, and magnesium. Chlorin, silicon, and sodium are essential to the full development of certain plants. Carbon is obtained from the carbon dioxid of the air; oxygen from the air and soil water; and hydrogen from the soil water that enters the plant through its roots. The other elements must be obtained from the soil. Since the compounds that contain these elements are usually solids, they can not be absorbed by the roots of the plant unless they dissolve readily in the soil water. Recent experiments show that manganese produces a decided effect upon the growth of plants. It appears to act as a stimulant in some cases, and in others as a real plant food.

371. Fertility of Soils.—A fertile soil contains all the elements essential to a proper development of plants. These elements must be in an available form. A poor soil is deficient in one or more important constituents needed for plant growth. A soil may lose its fertility: (1) by the continual removal of the essentials required by plants during successive harvesting of crops; (2) by the leaching out of the soluble matter by water. A loam containing

humus is generally a very fertile soil. The humus increases the capacity of a soil for holding water. It makes a clay soil more easily worked, and it supplies nitrogen for the growth of plants.

Nearly all soils contain sufficient silicon, iron, magnesium, sodium, chlorin, calcium, and sulfur to supply the needs of plants. For the growth of certain plants that require a large amount of sulfur and calcium, such as onions, garlic, cabbage, etc., the addition of a compound containing these elements is necessary. Calcium sulfate, often called land plaster, is the compound generally used. Most soils also contain nitrogen, phosphorus, and potassium. A sandy soil is apt to be deficient in potassium; soluble matter, or available mineral matter, is quite apt to be leached out of such a soil. On the other hand, potassium is very apt to be present in sufficient quantity in a clay soil. Feldspar contains potassium, and granite rocks generally contain considerable calcium phosphate. Limestone often contains fossils that furnish a soil with phosphorus from the bones of animals.



Fig. 105.—Effect of calcium carbonate in neutralizing the acidity of a muck soil, thus making the nitrogen available.

372. Fertilizers.—Fertilizers are often classed as natural and commercial. Before a farmer can tell just what fertilizers a soil needs, an accurate analysis of the soil must be made by a trained chemist. He can, however, by a systematic application of fertilizers for a period of

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several years, learn what elements the soil needs most. Soils are classed as alkaline, acid, or neutral, according to their reaction toward litmus. Acid soils are not suitable for the growth of certain plants, especially legumes and certain root-crops. The acidity of a soil may be corrected

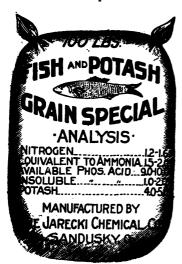


Fig. 106.—A fertilizer bag, showing analysis.

by the addition of lime. marl, or powdered limestone. Air-slaked lime is better than freshly prepared lime since it is not so caustic. and consequently not so likely to injure vegetation. Fig. 105 shows the effect of calcium carbonate upon the growth of cabbage in a very acid muck soil. letters on the pots show what fertilizers were used with the limestone. The results show the effect of neutralizing the acidity of the soil, thus making the nitrogen available. In Fig. 106 a fertilizer bag shows

the method of indicating the analysis of fertilizers. A complete commercial fertilizer contains potassium, nitrogen, and phosphorus.

### NITROGEN FERTILIZERS

Nitrogen.—Some of the sources of nitrogen were mentioned when we studied the element itself. Stable manure is rich in nitrogen, as is all decaying animal and vegetable matter. Such products as tankage, fish scrap, slaughterhouse refuse, dried blood, and guano are also extensively used. The sodium nitrate that is sold for fertilizer is

about 16 per cent. nitrogen; hence about 6 lb. of the nitrate are needed to furnish 1 lb. of nitrogen. It is very soluble in water so that it may be readily taken up by plants. It is more apt to be leached from the soils than some of the substances named above. This defect is overcome by using successive applications of the nitrate. Calcium nitrate is also used to some extent as a fertilizer. It contains



Fig. 107.—Effect of sodium nitrate upon the yield of wheat per acre.

a slightly higher per cent. of nitrogen than the sodium nitrate. Fig. 107 shows the effect of sodium nitrate on the growth of wheat.

Ammonium sulfate is a by-product obtained in making coal gas. It contains more than 21 per cent. of nitrogen and it is readily soluble.

Calcium cyanamid (CaCN<sub>2</sub>) is a nitrogen compound that has come into more recent use as a fertilizer. It is not so soluble as either the nitrates or the ammonium sulfate

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mentioned above, but it has the advantage of being less easily washed out of the soil. In the soil it undergoes chemical changes that convert it into ammonium compounds. Hot water acts upon it to form ammonia.  $CaCN_2 + 3H_2O \rightarrow 2H_3N + CaCO_3$ . The calcium that it

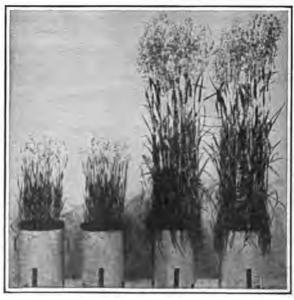


Fig. 108.—Oats grown with and without calcium cyanamid as a fertilizer.

(Permission of Scientific American.)

contains may be useful in neutralizing an acid soil. See Fig. 108, which shows the effect of calcium cyanamid upon the growth of oats.

## PHOSPHORUS FERTILIZERS

Rock phosphates which are found in Florida, Tennessee, and South Carolina, are phosphates of calcium. Some of the Western States also contain deposits of rock phosphate.

The origin of such deposits is probably from the fossil remains of the bones of pre-historic animals. To render these phosphates soluble they are treated with sulfuric acid.

The bones of slaughtered animals are ground and made into fertilizers. The principal mineral matter is calcium phosphate. Both fish scrap and guano also contain phosphorus.



No Acid Sodium Slag Slag Rock Double No Phos. Phos. Phos. Super Phos. Super Phos. Super Phos.

Fig. 109.—Effect of various phosphates on the growth of buckwheat.

The phosphorus that is present in iron ores is removed in the slag when the iron is made into steel. This phosphate slag is a valuable source of phosphorus for use in fertilizers. Fig. 109 shows the effect of various phosphates on the growth of buckwheat. The acid phosphate, the superphosphate, and the slag are more soluble, hence of more value for immediate use. The rock phosphate shows only a little more than half the increase over the check that the acid phosphate does.

## POTASSIUM FERTILIZERS

The most abundant supply of potassium is found at Stassfurt, Germany. The chlorid of potassium is the 322 SOILS

cheapest potassium compound that is available for plant food, although the sulfate is quite extensively used. The chlorid is more than 52 per cent. potassium; the sulfate contains nearly 45 per cent. potassium.

Sea-weeds contain large quantities of potassium and their ash makes an excellent fertilizer. Attempts are being made to develop a process of obtaining potassium from sea-weeds on a commercial scale. Wood ashes contain potassium carbonate which is a very valuable fertilizer, although the supply is limited.

Feldspar rocks contain an abundant reserve supply of potassium. This rock weathers too slowly to meet the demand for potassium when the soil is under constant cultivation. No commercial method of rendering the potassium in feldspar immediately available is in use. Generally the bags in which commercial fertilizers are shipped contain a printed analysis of the valuable constituents.

# SUMMARY

The process of changing bed-rock into mantle rock, or soil, is known as weathering. If the soil remains where it was formed it is called residual soil.

Soils are known as sandy, limy, or clay, depending upon the nature of the rock from which they are formed. Loam is a mixture of sand and clay. Decaying vegetable matter in the soil form's humus.

Plants need hydrogen, oxygen, carbon, nitrogen, potassium, phosphorus, sulfur, magnesium, calcium, iron, sodium, chlorin, and silicon for growth. The first three are obtained from water and the air; the last three are less important and are generally present in all soils.

A fertile soil contains all the above elements in a form that makes them available for plant use. It should not be acid. Lime and powdered limestone are valuable for neutralizing the acidity of soils.

The elements that are apt to be lacking in a soil are nitrogen, potassium, and phosphorus. These may be added from time to time in the form of soluble compounds of these elements known as commercial fertilizers.

The sources of nitrogen include plant and animal refuse, sodium nitrate, calcium nitrate, ammonium sulfate, and calcium cyanamid.

Phosphorus for use in making fertilizers is obtained from rock phosphates, ground bone, phosphate slag, guano, and fish scrap.

Potassium comes from sea-weed, wood ashes, and the deposits of potassium chlorid and sulfate found in Germany.

# **QUESTIONS**

- 1. How does the amount of rainfall affect the fertility of the soil?
- 2. Why is the soil of river bottoms so fertile? Recall the effect of the overflow of the Nile upon the fertility of the soil in Egypt.
- 3. How does the nature of the sub-soil affect the ability of a soil to retain mineral matter to be used as plant food?
- 4. Why does letting a soil lie idle during the summer (summer fallow) improve its fertility?
- 5. Why is a loam generally a fertile soil? Would you expect a loam to be easily tilled?
- 6. What danger arises from too frequent addition of lime to soils?
  - 7. What do you understand by a complete fertilizer?
- 8. Why is sulfuric acid used so extensively in the fertilizer industry?

# CHAPTER XXXV

# THE IRON FAMILY

373. The Family.—This family includes iron, nickel, and cobalt. Iron is the most important metal known from an industrial standpoint. The three elements in this group have similar chemical properties and form analogous compounds. Their valence may be either 2 or 3.

# IRON AND STEEL

374. Composition, Properties, and Uses of Cast Iron, Wrought Iron, and Steel.—In the chapter on metallurgy we learned that iron is extracted from its ores by reduction with carbon. As the iron comes from the blast furnace it contains considerable carbon and it is known as pig iron or cast iron.

Cast iron contains from 2 to 6 per cent. of carbon, which may be chemically combined with the iron to form an iron carbid, or it may exist uncombined as graphite. In the former case it forms a very hard white cast iron. In the latter case the iron is softer and gray in color. Traces of sulfur, phosphorus, and silicon are also found in cast iron Cast iron is hard, crystalline, and brittle. as impurities. It is neither malleable nor ductile. It can neither be welded nor tempered. Although it is not very tenacious, it can sustain very great weights without being crushed. Since it melts at a lower temperature, 1200°C., than any other form of iron, it is especially suitable for making castings. The molten cast iron is poured into a mold lined with sand and allowed to solidify.

Wrought iron is the purest form of commercial iron. It contains less than 0.3 per cent. carbon. It is made by a process known as puddling. This consists of heating cast iron in a reverberatory furnace (see Fig. 110) lined with iron oxid. The impurities in the cast iron are gradually oxidized and disappear as gaseous products, or they combine with the basic lining of the furnace. The molten iron is

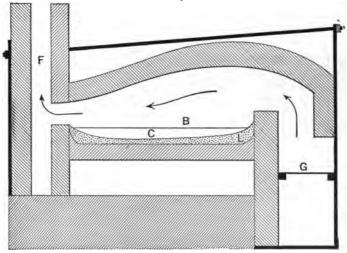


Fig. 110.—Reverberatory furnace. G, Grate; C, Charge; L, The lining; and F, The flue. Heat is reflected down upon the charge at B.

stirred until it becomes pasty, due to the fact that pure iron has a higher melting point than cast iron, and then worked into large balls called *blooms*. These blooms are removed from the furnace and worked under a trip-hammer to free them from slag. Wrought iron is soft, fibrous, ductile, and malleable. It can be welded, since it does not have a sharp melting point, but softens gradually. It can not be tempered. It is very tenacious. Since it is easily worked, it is used as blacksmith iron, for chains, and wire.

Steel is intermediate in composition between wrought iron and cast iron. It contains from 0.2 to 2 per cent. carbon. Generally its hardness increases with the increase in the per cent. of carbon it contains. Steel has the highest tensile strength of the known metals. It is ductile and malleable; it can be welded and tempered. More than 30,000,000 tons of steel were manufactured in the United States in 1912. Thousands of tons are used in the manufacture of automobiles, rails, railway carriages, armor plate, guns, projectiles, bridge material, and other structural steel.



Fig. 111.—One of the melting furnaces used for making crucible steel. (Courtesy of the Crucible Steel Company of America.)

375. Manufacture of Steel.—Since steel is intermediate in carbon composition between cast iron and wrought iron, it may be manufactured from either one of these substances. If it is to be manufactured from cast iron, as is more often the case, some method must be used to remove the excess

carbon. If wrought iron is to be the starting point, carbon must be introduced to give the desired composition. Both principles are in use. The Bessemer and the open-hearth processes use cast iron for making steel. The crucible and cementation processes start with wrought iron.

376. Crucible Process.—In this process of making steel wrought iron, scrap steel, and carbon are heated in graphite crucibles until the melting point is reached. The temperature is then maintained until the iron has absorbed enough carbon from the graphite, coke, or charcoal introduced, and from the crucible itself to give a steel of the desired

composition. The time required is from 3 to 4 hours. As each crucible holds only about 80 lb., the process is expensive, but it yields a very high-grade product, suitable for tool steel, springs, needles, pens, and cutlery steel (see Fig. 111).

# 377. Cementation Process. —In this process wrought iron bars are packed in charcoal and heated for several days at a yellow heat. The iron does not melt, but it slowly absorbs carbon from

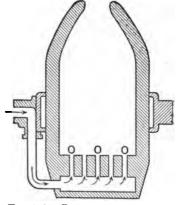


Fig. 112.—Bessemer converter, erect.

the charcoal. The steel is high-grade, but the time required for making it makes it an expensive process.

378. Bessemer Process.—In this process pig iron direct from the blast furnace is poured into a large egg-shaped "converter" that holds from 10 to 15 tons. The converter is built of wrought-iron plates and lined with fire-brick. The bottom contains holes through which air blasts enter in such a manner that the air finds its way up through the

molten iron in many fine jets (Fig. 112). The oxygen combines with the carbon and other impurities of the cast iron leaving the iron nearly pure. The blast lasts for 10 to 15

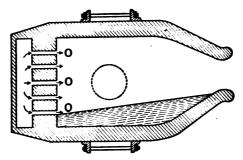


Fig. 113.—Bessemer converter, on its side.

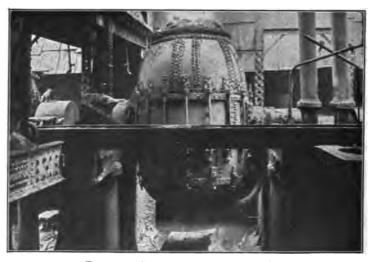


Fig. 114.—Bessemer converter, in action.

minutes. The converter is then turned down on its side (Fig. 113) and *spiegeleisen*, an iron rich in carbon and manganese, is added. The blast is then renewed long

enough to thoroughly mix the spiegeleisen with the contents of the converter. The manganese unites with the oxygen and prevents the formation of "blow-holes" in the steel (see Fig. 114).

The Thomas-Gilchrist process is a modification of the Bessemer process. It differs since the converter is lined with some basic material, such as limestone, to absorb the sulfur and phosphorus contained in the iron, since these substances make steel brittle.

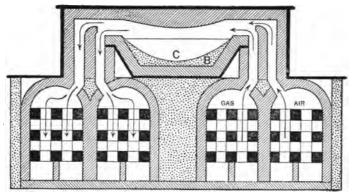


Fig. 115.—Open hearth process of making steel.

379. The Open-hearth Process (Siemens Martin).— The open-hearth furnace (see Fig. 115) consists of a large bed, or hearth, in which the charge, consisting of cast iron, scrap steel, and iron ore, is placed. The charge is heated by gas, both the gas and the air with which it combines being preheated as they enter the furnace through a checker work of hot fire-brick. This gives a much hotter flame than could be produced by burning the cool gas. The hot products of combustion pass out through a similar checker work on the other side of the furnace, thus heating it to a high temperature. The valves are then reversed so the gas and



Fig. 116.—Pouring the molten steel into the ingot molds.

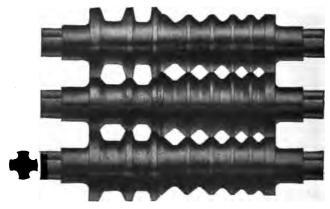


Fig. 117.—Roughing rolls for making bars for shrapnel. (Courtesy of Scientific American.)

air may enter through the checker work just heated. In such a regenerative furnace the fuel and air enter alternately from the sides of the furnace, one side being always heated by the products of combustion as the other is being used by the entering gases. The reversal of the valves occurs about every 20 minutes. The process requires from 6 to 12 hours. Although this process requires much longer than the Besse-



Fig. 118.—Steel ingot about to enter rolls.

mer process, it can be better controlled, resulting in the production of a more uniform steel. The charge varies from 50 to 100 tons. It is quite economical since the oxygen from the ore is being utilized to remove the carbon from the cast iron. Phosphorus is removed by lining the hearth with some basic material. Fig. 116 shows the pouring of ingots. The ingot is stripped, heated to the proper temperature, and then rolled into the desired shape (Figs. 117 and 118).

- 380. Purification of Steel.—In making steel there is always a tendency toward the formation of oxids near the end of the process. Gases in the steel also tend to form blow-holes. Both these defects are remedied by the addition of some metal that has a strong affinity for oxygen. Aluminum, titanium, manganese, and vanadium are used as purifiers. Titanium is especially desirable, and may be added to the extent of 10 to 15 per cent. It unites with both nitrogen and oxygen that may be present and gives a very homogeneous steel. The wearing qualities may be increased 40 per cent. by the use of this purifier.
- 381. Tempering of Steel.—The properties of steel depend not only upon the per cent. of carbon it contains but also upon the manner in which this carbon is held. *Mild steel* having as low as 0.2 per cent. carbon resembles wrought iron. *Low-carbon steel* contains from 0.2 to 0.8 per cent. carbon, so small an amount that it can not be tempered. *High-carbon steel* contains 0.8 to 2 per cent. carbon.

If high-carbon steel is heated above 670°C., iron carbid is formed which goes into solution in the iron. If this solid solution is cooled quickly by plunging it into cold water or oil, the carbid does not separate and a very hard steel is the result. If it is cooled slowly, however, a mixture of iron carbid, iron, and graphite results. This product is soft and tough. All grades of hardness between these extremes may be obtained by reheating a hardened steel to a definite temperature and then cooling it slowly. This process is known as tempering. If during the re-heating the temperature is only slightly raised and the product then cooled, a very hard brittle steel is produced, since very little of the hard iron carbid separates from the solid solution. If heated to a temperature nearer 670°C., a soft, tough steel will be produced upon cooling.

382. Special Steels.—Certain metals added to steel form alloys that have special properties fitting them for par-

ticular uses. These metals are generally added to the steel just before it is drawn from the furnace.

Nickel steel may contain as high as 4 per cent. of nickel. It does not corrode and it is very hard. It is used for making armor plate.

Nickel-chromium steel contains both nickel and chromium. This steel is very hard and tough, suitable for use as armor plate and for projectiles.

Manganese steel is exceedingly hard even when cooled slowly. It is used for making burglar-proof safes. It is nearly impossible to drill a hole in a good manganese steel safe.

Tungsten steel contains tungsten and generally some chromium. It is used for lathe tools, since it may be heated red hot without losing its temper. In metal turning a much higher speed may thus be used.

Chromium-vanadium steel has a very high tensile strength. It is used for automobile parts where the steel is subjected to severe strains and shocks. A good vanadium steel is so flexible that it may be bent nearly double without breaking.

383. Properties of Iron.—Ordinary iron is a grayish-white metal. It corrodes or rusts in moist air, the final product being a hydrated oxid. The rust is brittle and scales off, exposing the metal underneath; thus iron is not self-protective. In fact the rust seems to act like a catalytic agent to promote further corrosion. Rusting is accelerated by the presence of acids but retarded by alkalis.

Dilute acids act on iron with the liberation of hydrogen. Concentrated nitric acid does not act readily on iron, although dilute nitric acid acts upon it energetically. Alkalis have almost no effect on iron.

384. Protection of Iron from Corrosion.—Several methods for the protection of iron are in use. We have seen that

iron may be protected by galvanizing, or covering it with a layer of zinc. Iron may also be covered with a layer of tin, or it may be plated with nickel. Aluminum paint serves as a protection. Iron that is kept well-painted does not rust. Ironware is often protected by covering its surface with lacquer or enamel. Several alloys of iron that resist corrosion in moist air or in the presence of certain acids are now on the market. Silicon is a constituent of some of these alloys.

385. Oxids of Iron.—Three oxids of iron are known. Ferrous oxid, FeO, can be prepared but it changes rapidly in the air to ferric oxid, Fe<sub>2</sub>O<sub>3</sub>. This oxid is the most important ore of iron. It is used as a cheap red paint under the name of red ocher, Venetian red, or Indian red. Rouge is a form of ferric oxid used as a pigment and for polishing. Limonite is a natural hydrated ferric oxid used as a pigment under the name yellow ocher. When calcined it forms the siennas and umbers. When iron burns in oxygen a ferrosoferric oxid, Fe<sub>3</sub>O<sub>4</sub>, is produced. It is black and magnetic. The scale that peels off when blacksmith iron is worked consists of this oxid. Since a thin film of this oxid is adherent, it forms a protective coat. Under the name of Russia iron it is artificially produced on locomotives, stove-pipes, etc., to prevent corrosion.

386. Oxidation and Reduction as Related to Changes of Valence.—Two chlorids of iron are known; ferric chlorid, FeCl<sub>3</sub>, and ferrous chlorid, FeCl<sub>2</sub>. If we treat ferric chlorid with nascent hydrogen it is reduced to ferrous chlorid, or the valence of the iron is lowered from 3 to 2:

$$Fe'''Cl_3 + (H) \rightarrow Fe''Cl_2 + HCl.$$

Since no oxygen is abstracted from the compound, as in the narrower sense of reduction, we may broaden the definition of reduction to include any chemical reaction that involves a lowering of the valence of a positive element. From the standpoint of the ionic theory, reduction is accomplished when an ion loses a positive charge, or gains a negative charge:

$$Fe^{+++} - (+) \rightarrow Fe^{++}, \text{ or } Fe^{+++} + (-) \rightarrow Fe^{++}.$$

Conversely, by heating ferrous chlorid with an oxidizing agent in the presence of hydrochloric acid, ferric chlorid is produced:

$$2\text{FeCl}_2 + 2\text{HCl} + (O) \rightarrow 2\text{FeCl}_3 + \text{H}_2\text{O}.$$

In this case the valence of the iron is increased from 2 to 3. Oxidation may be defined as a chemical action that involves an increase in the valence of the positive element. According to the ionic theory, an ion is oxidized by gaining a positive charge or by losing a negative charge:

$$Fe^{++} + (+) \rightarrow Fe^{+++}, \text{ or } Fe^{++} - (-) \rightarrow Fe^{+++}.$$

Ferrous salts are always formed by the action of very dilute acids since the hydrogen liberated keeps them reduced. Ferric salts are always formed when oxidizing agents are present. Thus moderately concentrated nitric acid always forms ferric salts.

Ferric chlorid is used in medicine. Absorbent cotton dipped into a solution of ferric chlorid is known as *styptic cotton*. When put on a wound it stanches the flow of blood and also serves as an antiseptic.

- 387. Ferrous Sulfate.—FeSO<sub>4</sub>. Large quantities of ferrous sulfate are obtained as a by-product by concentrating solutions used for cleaning iron and steel that is to be dipped or plated. It forms light green crystals known as *copperas* or *green vitriol*. It is used as a mordant, as a spray for destroying weeds, and in making ink.
- 388. Inks.—If we add to a freshly prepared solution of ferrous sulfate a solution of tannic acid, the nearly colorless compound, ferrous tannate, is formed. It slowly oxidizes to form the black compound, ferric tannate. Iron inks contain ferrous tannate, dextrin, some poisonous com-

pound to prevent the growth of mold, and usually a little dye to give the ink a temporary color until the ferrous tannate is oxidized to ferric tannate to produce a permanent color. Many of the inks now used are solutions of aniline dyes. A third class of inks, of which printer's ink is a common example, is made from lamp-black and some material to serve as a binder. Iron inks are easily removed by the use of a reducing agent, but the other types can not be removed by this method.

389. Tests for Iron.—If we add to a solution of a ferrous salt a few drops of a solution of potassium ferricyanid, K<sub>2</sub>Fe(CN)<sub>6</sub>, commonly called red prussiate of potash, a dark blue precipitate is formed. This blue substance is known as ferrous ferricyanid; it is used as a pigment under the name of Turnbull's blue. Since the reaction occurs only when ferrous ions are present, it serves as a test for ferrous iron.

$$3\mathrm{FeCl_2} + 2\mathrm{K_3Fe(CN)_6} \rightarrow \mathrm{Fe_3[Fe(CN)_6]_2} + 6\mathrm{KCl}.$$

A dark blue precipitate is also obtained by mixing solutions of a ferric salt and potassium ferrocyanid, K<sub>4</sub>Fe(CN)<sub>6</sub>, or the yellow prussiate of potash.

$$4\text{FeCl}_3 + 3\text{K}_4\text{Fe}(\text{CN})_6 \rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_8 + 12\text{KCl}.$$

This reaction takes place when ferric ions are present and serves as a test for ferric iron. The precipitate, known as Prussian blue, is used as a pigment. It is sometimes used as laundry blue. If the clothes have not been rinsed free from alkaline soaps, their alkalis will decompose this blue compound precipitating ferric hydroxid on the fibers and forming iron rust spots.

390. Blue-prints.—Solutions of ferric salts form only a brown solution when mixed with potassium ferricyanid. Blue-prints are made by coating in the dark a well-sized paper with a mixture of the solutions of ferric ammonium

citrate and potassium ferricyanid. After the paper is dry it is then placed under the negative and exposed to the light. Wherever the light strikes the paper, reduction occurs and a ferrous salt is produced. The reduction proceeds more rapidly where the light is strongest. The print is developed by dipping it into water, when the ferrous salt unites with the ferricyanid to form Turnbull's blue. Where no light strikes the print, no reduction occurs and the water washes away the unchanged mixture, thus fixing the print. The exposed portions will be blue in color and the unexposed parts will be white.

## NICKEL

391. Nickel.—Ontario, Canada, produces large quantities of nickel. It is a hard, silver-white metal, capable of receiving a high polish. It does not tarnish easily. Otherwise its chemical properties are similar to iron.

Nickel is used for making steel, as a covering or plate for other metals, and as a constituent of certain alloys. *Nickel coins* are about 20 per cent. nickel, the remaining constituents being mostly copper.

Nickel forms two classes of salts, nickelous, in which the valence is 2; and nickelic, having a valence of 3. The former are more common; they usually crystallize as beautiful green crystals. The principle of oxidation and reduction, or an increase and decrease in the valence of nickel and iron, is used in the Edison storage battery.

## COBALT

392. Cobalt.—Cobalt so closely resembles nickel that these elements are frequently spoken of as the twin metals. Metallic cobalt has little or almost no use. Attempts are being made to use it in place of nickel for electroplating metals. It gives a more durable, but more expensive, plate.

Like nickel and iron, cobalt has a valence of either 2 or 3. The *cobaltous* compounds, which exist as red crystals that

form pink or red solutions are the more common. cobalt compounds are red when hydrated and blue when anhydrous, cobalt chlorid, CoCl2, is used as a rather crude method of determining the amount of moisture the air contains. Substances dipped in its solution change color as the moisture in the air varies. When the relative humidity is high they are pink in color; as the air grows less moist they change to a lavender or blue color. As the blue color is far more intense than the red, cobalt salts form the basis of the so-called sympathetic or invisible inks. The writing which is done with a dilute solution is almost colorless until heat is applied when the more intense blue color shows clearly. Cobalt nitrate, Co(NO<sub>3</sub>)<sub>2</sub>, finds some use in ana-Cobalt compounds impart to glass a beautiful lytical work. blue color.

# SUMMARY

Steel may be made from wrought iron either by the crucible process or the cementation process. Both processes depend upon the absorption of carbon by the heated iron.

Steel is also made from cast iron by the Bessemer and the open-hearth processes. In the Bessemer process the excess carbon is all burned out by an air-blast, and spiegeleisen then added to introduce manganese and the proper per cent. of carbon.

In the open-hearth process cast-iron is heated with iron ore until a steel of the desired carbon content is obtained. The process is slow enough so the product may be tested periodically.

When steel is heated and then cooled quickly it is very hard and quite brittle. If cooled slowly it becomes soft and tenacious. When it is heated a second time to a certain temperature and then cooled properly, a process known as tempering, steel of any desired degree of hardness between these extremes is produced. Ordinary iron rusts in moist air forming a hydrated oxid. Iron may be protected by covering it with zinc, tin, or nickel. Aluminum is used as a protective paint. Other methods of protecting iron include the use of lead paints, lacquers, and enamels A thin adherent film of magnetic oxid of iron forms when iron is treated with superheated steam. Iron covered with such a protective coat is known as Russia iron.

Any chemical change that involves a decrease in the valence of the positive element of a compound is reduction. Oxidation causes the valence of the positive element to be increased.

Ferrous sulfate is used as a mordant, as a spray for weeds, and in the manufacture of ink.

A ferrous salt gives a blue color with a ferri-cyanid; a ferric salt gives a blue color with a ferro-cyanid.

	Carbon content, per cent.	Structure	Hardness	Properties
Cast iron	2–6	Crystalline	Very hard	Can not be weld- ed or tempered
Wrought iron	0.05-0.3	Fibrous	Soft	Can be welded, but not tem- pered
Steel (low-carbon)	0.2 -0.8	Granular	Moderate	Can be welded, but not tem- pered
Steel (high-carbon)	0.8 -2	Granular	Hard	Can be welded and tempered

PROPERTIES OF IRON AND STEEL

# **QUESTIONS AND PROBLEMS**

1. Why can not wrought iron be tempered? Why can not cast iron be welded? Why is it more difficult to weld a high-carbon steel than it is to weld a low-carbon steel?

- 2. How many pounds of iron can be obtained from 1 ton of hematite, Fe<sub>2</sub>O<sub>3</sub>, if the ore is 90 per cent. pure? How many pounds of the chlorid of iron could be obtained by dissolving all this iron in hydrochloric acid?
- 3. Compare cast iron, wrought iron, and steel as to composition, properties, and uses.
  - 4. What is the function of a "purifier" in the making of steel?
  - 5. Why would you not expect iron to occur native?
- 6. How would you convert ferric chlorid into ferrous chlorid? How would you change ferrous chlorid to ferric chlorid?
- 7. Which class of iron compounds would you expect to be more stable when exposed to the air? Which would be the more stable, the solid salts or their water solutions?
- 8. If you were given an iron solution how would you determine whether it contains ferrous or ferric iron?
- 9. Freshly prepared ferric hydroxid is an antidote for arsenic poisoning. How would you prepare this compound? Write the equation for the reaction.
- 10. How would you remove a stain made with an iron ink? Would the same method be applicable for removing rust spots made with Prussian blue in the laundry?

Topics for Reference.—Heroult's electric furnace for making steel. Comparison between Bessemer and open-hearth processes of making steel. Use of oxidation and reduction in Edison storage battery.

# CHAPTER XXXVI

# THE COPPER FAMILY

393. The Family.—The copper family includes copper, silver, and gold. All of these metals are found free in nature to some extent. They are all soft heavy metals, ductile and malleable. All are excellent conductors of heat and electricity.

## COPPER

394. Copper.—Quite large quantities of copper are found native, sometimes in masses of scores of tons (Fig. 119). The sulfid and carbonate are also quite abundant. The sulfid and carbonate ores of copper are subjected to a preliminary roasting, and the copper is then extracted by reduction with carbon. It is refined by electrolysis (Fig. 120).

Copper is a rather soft, red metal. It is ductile, malleable, and very tenacious. Its specific weight is 8.9. As a conductor of heat and electricity, copper stands next to silver.

Heated in the air, copper forms the black cupric oxid, CuO; its vapor burns with a green flame. Exposed to the action of sulfur fumes, copper soon becomes covered with a blue-black coating of copper sulfid, CuS. Copper tarnishes in moist air, a green basic carbonate often being produced. It is self-protective as the tarnish is adherent. Hydrochloric acid does not affect copper, nor does dilute sulfuric. Nitric acid and hot concentrated sulfuric acid, acting as oxidizing agents, attack copper forming the nitrate and

sulfate respectively. The soluble compounds of copper are poisonous.

395. Uses.—Copper is extensively used for making electrical conductors. It also finds use for sheathing ships, for making electrotypes, and in several alloys.

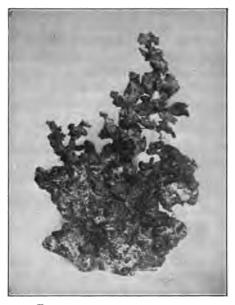


Fig. 119.—Mass of native copper.

Brass is an alloy of copper and zinc; bronze contains tin in addition to these elements; German silver contains copper, zinc, and nickel. All the coins contain some copper, the copper coins as high as 95 per cent.

396. Compounds.—Copper forms cuprous and cupric compounds. In cuprous oxid, Cu<sub>2</sub>O, the valence is 1; in cupric oxid, it has a valence of 2. The cupric compounds are the more important. Copper sulfate, CuSO<sub>4</sub>, is the most important compound of copper. It forms large blue

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crystals having the formula CuSO<sub>4</sub>·5H<sub>2</sub>O. It is generally known as blue vitriol, or bluestone. Copper sulfate finds use as a mordant in calico printing, in voltaic cells, for copper plating and electrotyping, and as a fungicide and insecticide. For spraying fruit trees and grapevines, it is generally used in the form of Bordeaux mixture, a preparation made by mixing a solution of copper sulfate with slaked lime.

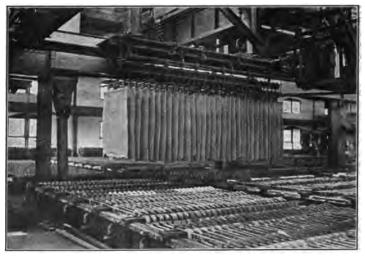


Fig. 120.—Refining copper by electrolysis. A set of electrodes lifted from the electrolytic tank is shown at center.

# SILVER

397. Properties of Silver.—Silver is a soft, white, lustrous metal. It is very ductile and malleable. Its specific weight is 10.5. Of all the metals silver is the best conductor of heat and electricity.

Silver is an inactive metal, since is does not oxidize even in moist air. If the air contains traces of sulfur, however, a brownish-black tarnish of silver sulfid is readily formed. Silver dissolves readily in nitric acid and in hot concentrated sulfuric. Hydrochloric acid does not attack it, nor does dilute sulfuric acid.

- 398. Uses.—Silver is used in jewelry and coins. The U.S. silver coins contain 90 per cent. silver and 10 per cent. copper. The British coins contain 92.5 per cent. silver. Sterling silver is an alloy having the same per cent. of silver as the British coins. Large quantities of silver are used for plating tableware. In silvering mirrors, advantage is taken of the fact that silver compounds are easily reduced, the silver being deposited on the glass as the reduction occurs.
- 399. Silver Compounds.—Silver nitrate, AgNO<sub>3</sub>, crystallizes in colorless scales. Under the name of *lunar caustic* it is sometimes used by surgeons for cauterizing abnormal growths. *Oxidized silver* is a sulfid of silver made by dipping the metal into a solution of a sulfid, usually of sodium or ammonium. Silver chlorid, AgCl, silver bromid, AgBr, and silver iodid, AgI, are all sensitive to light when organic matter is present. The action is one of reduction, the metallic silver that is formed being finely divided and dark in color. These compounds are used in photography.
- 400. Photography.—The main steps in the chemistry of photography consist: (1) in preparing the negative; (2) in making the print. In the preparation of the negative there are three important operations: (1) the exposure; (2) developing; (3) fixing. The plate used for making the negative is prepared by covering a glass plate or celluloid film with gelatine containing silver bromid in suspension. This plate is exposed to the light just long enough to start the reduction of the silver bromid. It is then treated in a dark room with a developer, which consists of rather mild reducing agents, such as hydroquinone and pyrogallol. The developer can not start the reduction of the unchanged silver salt, but it can continue the reduction begun by the

action of the light. After the developing process has proceeded far enough, the plate or film is then put in a strong solution of sodium thiosulfate, commonly known as hypo. This solution dissolves the unchanged silver salt so the plate will not darken when again exposed to the light. The "hypo" thus serves as a fixer. The more intense the light the more rapidly the reduction occurs. White reflects more light than colored objects, hence white objects make the plate very dark and vice versa. For these reasons the plate is now called a negative (Fig. 121).

In making the print, a well-sized paper sensitized in the same manner as the plate, is covered by the negative and then so exposed that the light must pass through the negative. Here the dark part of the negative cuts off the more light and the intensity of reduction is just the reverse from that in the production of the negative, and a positive print is produced (Fig. 122). The print is developed and fixed in the same manner as the plate. It is often toned by dipping it into a solution of the salts of gold or platinum. The silver goes into solution replacing these metals thus giving a richer color to the print.

## GOLD

401. Gold.—Gold is a soft, yellow metal, very ductile and malleable. It is nearly twice as heavy as silver, its specific weight being 19.3. Gold does not tarnish when exposed to the air, and is generally a very inactive metal. No single common acid affects gold, but it dissolves readily in a mixture of hydrochloric and nitric acids, or aqua regia.

Gold finds use in coins and jewelry. Since it is too soft to wear well, it is usually alloyed with copper. Its purity is expressed in *carats*, pure gold being 24 carats fine; 18-carat gold contains 75 per cent. gold and 25 per cent. copper. Gold coins are 90 per cent. gold and 10 per cent. copper.

Gold may have a valence of 1 in aurous compounds, or a valence of 3 in auric compounds. Auric chlorid, AuCl<sub>3</sub>,



Fig. 121.—A negative plate.

is one of the most important salts. It is used in photography. A double cyanid of gold and potassium is used for gold plating.

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# SUMMARY

Copper is a heavy, ductile metal used extensively for electrical conductors. When exposed to moist air a self-

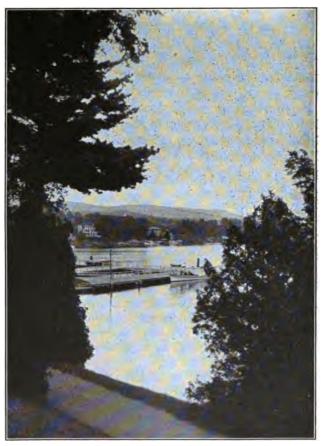


Fig. 122.—A positive print.

protective coat of the basic carbonate is formed. Nitric acid acts readily on copper.

Copper sulfate is used in batteries, for copper plating, for water purification, and as a fungicide and insecticide.

Silver is the best conductor of heat and electricity known. It is used in jewelry, in silver coins, and for plating tableware.

Silver salts are sensitive to light. Thus they find use in photography. Two important steps in photography consist: (1) in making the negative; (2) in making the print.

In making a negative there are three operations: (1) the exposure, which starts the reduction of the silver salt; (2) the developing, which continues the reduction; (3) and the fixing, which removes the unchanged silver salts and makes the negative permanent.

The same operations are used in making the print; it is frequently toned by replacing the silver on the print with gold or platinum.

Gold is a valuable yellow metal. It does not tarnish hence it is suitable for use in making coins and jewelry. Pure gold is 24 carats fine.

## **QUESTIONS AND PROBLEMS**

- 1. Why is copper not suitable for making cooking utensils?
- 2. If dilute sulfuric acid does not act on copper, explain how copper sulfate can be made by putting copper shot in a lead basket and alternately dipping them in warm dilute sulfuric acid and then suspending them in the air.
- 3. How could scrap iron be used to recover copper from the waste waters of copper mines?
  - 4. How could you tell gold from brass?
- 5. By the aid of a labelled diagram, outline a method of plating tableware with silver.
- 6. How much copper sulfate could be obtained from 10 lb. of copper? If copper is worth 20 cents per pound and sulfuric acid 1 cent per pound what will it cost to make 1 lb. of crystallized copper sulfate, exclusive of labor?

- 7. Why is silver-plated ware more easily scratched than sterling silver?
  - 8. Why is silverware tarnished by mustard or eggs?
- 9. Tarnished silverware may be cleaned by putting it in an aluminum pan containing boiling water and a little baking soda. Explain.
- 10. Which forms the better coating for mirrors, silver or tin amalgam? Why?
- 11. Why should gold rings not be permitted to come into contact with mercury?
  - 12. How could gold be recovered from gold chlorid?
- 13. Can you give a reason for the use of silver salts in making indelible inks?
- 14. Why have copper, silver, and gold been known for centuries, while such metals as sodium and potassium are comparatively new metals?

Topics for Reference.—Calumet and Hecla copper mine. Mining and extracting gold. Touchstone test for gold. Why an electroplater should know Faraday's laws.

# CHAPTER XXXVII

### TIN AND LEAD

402. Introductory.—Chemically tin and lead resemble the non-metals carbon and silicon. Tin occurs in nature mainly as the oxid, while the sulfid of lead is the most important ore.

#### TIN

403. Properties of Tin.—Tin is extracted from its oxid by reduction with carbon. Tin is a soft white metal, a little lighter than iron. It has a very low melting point, 232°C. The pure metal is known as block tin. It is so malleable that it may be rolled into very thin sheets, forming tin foil.

Air and water do not act on tin at the ordinary temperature. Dilute acids have little effect on tin, but concentrated acids attack it readily. With hydrochloric acid it forms stannous chlorid. Sulfuric acid forms a sulfate of tin. The action of nitric acid on tin is very peculiar. Instead of a nitrate being formed the tin is oxidized to form meta-stannic acid, H<sub>2</sub>SnO<sub>3</sub>, a white insoluble compound.

404. Uses of Tin.—Ordinary tinware, or tin plate, is made by cleaning sheet iron and dipping it into molten tin. Such tinned iron is used for making "tin" cans and cooking utensils. If the coat is thick enough it does not rust, but the iron rusts very rapidly as soon as the coating of tin is broken at any point, since the contact of two metals causes the more active one to corrode very rapidly. Tin foil usually contains some lead, especially the cheaper grades.

Pure tin pipes are used instead of lead as conduits for slightly acid liquids.

Solder is an alloy containing tin and lead. The other alloys of tin, such as bronze, type-metal, anti-friction metals, and the fusible alloys, have been studied under other metals.

405. Compounds of Tin.—Stannous chlorid, SnCl<sub>2</sub>, is an important compound of tin. It is used as a mordant, since it forms very brilliant shades. Stannous chlorid is also used for weighting silks. It is a reducing agent. An interesting example of oxidation that does not involve a transfer of oxygen occurs when a solution of stannous chlorid is added to mercuric chlorid:

$$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + 2HgCl.$$

$$\downarrow$$
 $SnCl_2 + HgCl_2 \rightarrow SnCl_4 + Hg.$ 

In these interactions stannous chlorid acts as a reducing agent. The mercuric chlorid acts as an oxidizing agent. Stannic chlorid, SnCl<sub>4</sub> in which tin has a valence of 4, is formed and the bi-chlorid of mercury may be reduced to the mono-chlorid or to the metallic state. Stannic sulfid, SnS<sub>2</sub>, is used as a yellow pigment under the name of "mosaic gold." Meta-stannic acid is used to strengthen cotton fibers and to render them non-inflammable.

#### LEAD

406. Properties.—Lead is a soft bluish-white metal. Its specific weight is 11.3, it being heavier than most of the common metals. Lead is malleable, but not ductile. It may be made into wire, however, by forcing the heated metal through a die. Lead pipe is made in a similar way by forcing the metal through a ring-shaped opening.

Lead oxidizes quite rapidly, but the coating is adherent

and protects the metal underneath. Hydrochloric acid and sulfuric acid have little effect on lead, but nitric acid acts upon it vigorously. Acetic and other organic acids act readily on lead, and water containing carbon dioxid acts upon it slowly. As all soluble lead compounds are poisonous, lead is objectionable for use in making water pipes. Lead salts are especially dangerous even in small quantities as they are not readily excreted, but accumulate in the body. Painter's colic is a disease due to chronic lead poisoning.

407. Uses.—Enormous quantities of lead are used in making white lead paint. Sheet lead is used for lining the chambers of sulfuric acid plants and for the plates of storage batteries. Lead pipe is used as conduits for electrical wires; plumbers also use lead pipe since it is easy to cut, it may be readily bent into any desired shape, and its edges may be readily fused or soldered together to make a seamless joint. Lead foil is used for lining tea chests, and as a substitute for tin foil. Except for its weight, sheet lead makes excellent roofing material.

Shot is made from lead containing a trace of arsenic. The other alloys of lead, solder, type-metal, fusible metals, and anti-friction metals, have been studied under other titles.

- 408. Oxids of Lead.—Three oxids of lead are important: Lead monoxid, PbO, commonly known as litharge, is a yellow powder used in the glass, paint, and varnish industries. Lead dioxid, PbO<sub>2</sub>, is a brown powder used as an oxidizing agent. It is formed when storage batteries are charged, and becomes the positive plate. Red lead, or minium, is an oxid of lead having the formula Pb<sub>2</sub>O<sub>4</sub>. It is used as a red pigment. Mixed with linseeed oil it serves as an oxidizing agent, causing the oil to dry or harden rapidly.
- 409. White Lead.—Several processes are in use for making white lead. The Dutch process has been in use for

centuries and yields a very good product. In this process perforated lead discs (Fig. 123), or "buckles," are placed in earthenware pots containing a little dilute acetic acid. The pots are then placed in rows and covered with stable manure or with spent tan bark. Other tiers of pots are placed on the first ones and covered as before, until a considerable height is reached (see Fig. 124). The heat from fermentation vaporizes the acetic acid which acts on the lead to form a basic lead acetate. Carbon dioxid which

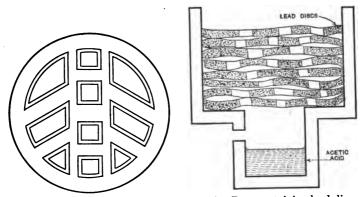


Fig. 123.-Lead disc.

Fig. 124.—Pots containing lead discs.

is liberated by the fermentation changes the acetate into a basic lead carbonate. The process requires 90 days or more. The aim is to produce a white lead having the formula  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ , but the product varies to some extent. White lead is ground very fine with linseed oil and used as a paint base.

- 410. Sublimed white lead is used as a paint base. It is made by roasting galena, PbS, at a high temperature. It contains lead sulfate and lead oxid. Some zinc oxid is usually added to it.
- 411. Lead Chromate.—PbCrO<sub>4</sub>. Lead chromate is used as a pigment; it is commonly known as chrome yellow.

### **PAINTS**

412. Paints.—A paint consists of: (1) a paint base; (2) a vehicle. It may also contain a pigment. A good paint base should be opaque even in thin layers; it should have durability, mix readily with the vehicle, and have a high covering power.

White lead answers all these requirements remarkably well, but it turns black when exposed to sulfur vapor due to the formation of the black lead sulfid, PbS. It also tends to become chalky with age.

Zinc oxid does not have so good a covering power as white lead. It tends to become brittle and scale off, or peel. It does not turn black when exposed to sulfur fumes since zinc sulfid is white.

Sublimed white lead, containing some zinc oxid, is coming into favor as a paint base. It is not affected by sulfur vapors. It is very durable and has good covering power. It is not so poisonous as white lead. Mixtures of white lead and zinc white form good paint bases since they combine the good qualities of each and to some extent neutralize the disadvantages.

Lithopone is a comparatively new paint base made by treating zinc sulfate with barium sulfid:

$$ZnSO_4 + BaS \rightarrow BaSO_4 + ZnS$$
.

It has a lustrous white color, and its covering power is good.

413. Vehicles.—Linseed oil is the vehicle most often used in paints. It is an unsaturated compound that "dries" by uniting with oxygen from the air to form a tough resin. Boiled linseed oil is made by heating the raw oil with oxids of lead or manganese. This treatment makes the oil harden or "dry" more rapidly.

Chinese wood oil is a vehicle used in enamel paints and

also for paints that are to be subjected to severe weather conditions.

The "driers" used in paints are made by heating a part of the oil with oxids of lead or manganese. They act as catalytic agents, giving up a part of their oxygen to hasten the "drying" and taking oxygen from the air again.

414. Pigments.—A pigment is some insoluble substance of high coloring power that is added to a paint base. A large number are used and their composition varies greatly. They include lakes, oxids and sulfids of metals, complex cyanids, etc. Chromium compounds are especially valuable as pigments.

Red pigments include red lead, red ocher, vermilion, and carmine, compounds already studied.

Blue pigments include such compounds as Prussian blue, ultramarine, and cobalt blue.

Yellow pigments include chrome yellow, yellow ocher, and litharge.

From combinations of these pigments and others not given here, the various shades may be produced.

415. Extenders or fillers are used in paints, especially in ready-mixed paints. They are cheaper substances than the paint bases and are often classed as adulterants. They often increase the durability of the paint, and they so completely fill the pores that the surface is more easily repainted. Kaolin, barium sulfate, calcium sulfate, and whiting, or calcium carbonate, are some of the most common fillers.

### SUMMARY

Tin is a soft, white, malleable metal. It does not tarnish in the air. Acids act upon it rather readily.

Tinware is sheet iron covered with a coating of tin. Tin foil finds considerable use as air-tight wrapping material.

Solder contains tin and lead. Other alloys of tin are bronze, type-metal, and anti-friction metal.

Stannous chlorid is used as a mordant and for weighting silks.

Lead is a soft, bluish-white metal. Exposed to the air it soon becomes covered with a protective layer of the oxid, Pb<sub>2</sub>O. Nitric acid and organic acids act readily on lead. Lead salts are very poisonous. Epsom salts forms a good antidote.

Lead is used for making paints. It is also used for making pipe, and as sheet lead. Shot, solder, type-metal, and the fusible alloys contain lead.

Litharge, PbO, and minium, Pb<sub>2</sub>O<sub>4</sub>, are oxids of lead used in the paint industry. Lead peroxid, PbO<sub>2</sub>, is used in storage batteries.

White lead is a basic lead carbonate that is used as a paint base. Sublimed white lead contains lead sulfate, lead oxid, and zinc oxid. Chrome yellow is a chromate of lead.

A paint consists of a paint base mixed with a vehicle. The most common paint bases are white lead, zinc white, mixtures of these two substances, sublimed white lead, and lithopone. The most common vehicles are linseed oil and Chinese wood oil.

A pigment is a highly colored substance sometimes added to a paint base to give it some desired shade or color. An extender is a cheap product often added to ready-mixed paints. They are often classed as adulterants, although they may increase the durability of the paint.

# QUESTIONS AND PROBLEMS

- 1. Which makes the better coating for iron, tin or zinc? Give a reason for your answer.
  - 2. How could tin be recovered from tin cans?
- 3. Tinware rusts rapidly as soon as a little of the iron is exposed. Explain.
- 4. Write the equation representing the reaction between solutions of stannous chlorid and auric chlorid.

- 5. Solutions of stannous chlorid do not keep well when exposed to the air. What two changes may occur? Would the addition of a little metallic tin and hydrochloric acid aid in preserving it?
  - 6. What is the chief objection to lead as a roofing material?
- 7. Can you see any reason why some countries restrict the manufacture and use of white lead?
  - 8. Compare zinc white and white lead as paint bases.
  - 9. What action occurs in the "drying" of a paint?
- 10. Would white lead be suitable for use in a chemical laboratory?
- 11. An American chemist won a prize for a method of restoring the color to some valuable paintings that had been darkened by sulfur vapors. He washed the paintings with hydrogen peroxid. Explain the chemical action.
- 12. How many pounds of lead can be obtained from 1000 lb. of galena, PbS?

Reference Topics.—Manufacture of shot. Tin disease.

## CHAPTER XXXVIII

# MANGANESE AND CHROMIUM

- 416. Introductory.—Although these two elements do not belong to the same family, they are often treated in the same chapter, since they resemble each other to some extent in chemical properties. Both elements are extracted by heating their oxids with aluminum. Both may act either as base-forming elements or acid-forming elements. The chief use of both metals is in the manufacture of steels that are very hard and tough. The valence of the elements varies, chromium having a valence of 2, 3, or 6. Manganese may have a valence of 2, 3, 4, 6, or 7.
- 417. Manganese Dioxid.—MnO<sub>2</sub>. Manganese dioxid, or the black oxid of manganese, is found in nature. It is used as an oxidizing agent, in making spiegeleisen and ferromanganese, in the preparation of chlorin, and to neutralize the green color imparted to glass by iron compounds. The valence of manganese in this compound is 4, but when it interacts with hydrochloric acid in the preparation of chlorin, there is an interesting change of valence:

$$MnO_2 + 4HCl \rightarrow MnCl_4 + 2H_2O \uparrow MnCl_2 + Cl_2.$$

When manganese acts as a base-forming element, its valence is usually 2. Thus any MnCl<sub>4</sub> that may have been formed breaks up as shown to form *manganous chlorid*, MnCl<sub>2</sub>. *Manganous* salts are pink in color.

418. Acid-forming Manganese.—By the use of oxidizing agents on certain manganese compounds it is possible to

produce manganates and permanganates. In these compounds the valence of manganese is 6 and 7 respectively; it acts as an acid-forming element in both cases. The manganates are quite unstable.

Potassium permanganate is the most important compound of acid-forming manganese. It is such a vigorous oxidizing agent that its concentrated solution can not be filtered through paper. It forms purplish-red solutions that are decolorized by reducing agents. It is extensively used in analytical work, especially in iron and steel analysis. In an acid solution it gives up its oxygen to a reducing agent as shown by the following equation:

 $2KMnO_4 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 3H_2O + 5(O).$ 

Potassium permanganate finds some use as a disinfectant and antiseptic. It is coming into favor as a bleaching agent.

#### CHROMIUM

- 419. Base-forming Chromium.—As a base-forming element, chromium may form chromous salts, in which its valence is 2, or it may form chromic salts, in which it has a valence of 3. The latter salts are analogous to the salts of ferric iron. They are green or violet in color and find use as pigments. Since they hydrolyze readily they form good mordants. Chrome alum, K<sub>2</sub>SO<sub>4</sub> · Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 24H<sub>2</sub>O, which is also used as a mordant, is formed by evaporating mixed solutions of potassium and chromium sulfates.
- 420. Acid-forming Chromium.—Chromic oxid, Cr<sub>2</sub>O<sub>3</sub>, may be oxidized to form CrO<sub>3</sub>, the anhydrid of the unstable chromic acid, H<sub>2</sub>CrO<sub>4</sub>. Chromic acid is a vigorous oxidizing agent. Several of its salts are quite important compounds. We have seen that lead chromate, PbCrO<sub>4</sub>, is an excellent pigment. Barium chromate, BaCrO<sub>4</sub>, is also used as a pigment. Potassium chromate, K<sub>2</sub>CrO<sub>4</sub>, is a yellow crystalline salt of chromic acid.

Potassium di-chromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, and sodium di-chromate, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, are orange-red crystalline compounds. It will be observed that chromium has a valence of 6 in both the chromates and di-chromates. If we write the formula of potassium di-chromate as K<sub>2</sub>CrO<sub>4</sub>·CrO<sub>3</sub>, the relation between the chromates and the di-chromates is apparent. The di-chromates are excellent oxidizing agents. Potassium di-chromate is used in photogravure and half-tone work, since it forms an insoluble compound with gelatine or asphalt when exposed to the light. It is also used in tanning light leathers since it shortens the process from several weeks, or months, to only a few hours.

421. Leather is made from the skins of various animals. The hair is first removed by the use of lime. Next the skin is treated with a dilute acid to neutralize the lime and to cause the skin to swell, the process being known as plumping. Tanning changes the skin into leather so that it becomes impervious and does not putrefy. Tan bark from hemlock and other woods produces this change slowly and is the substance used for heavy leathers. Potassium di-chromate produces the same change in the presence of a reducing agent by precipitating chromic hydroxid, Cr(OH)<sub>3</sub>, in the leather. The leather is then worked with oil to make it soft and less porous.

## SUMMARY

Manganese and chromium are used in making special steels.

Manganese dioxid is an oxidizing agent; it is used in the glass industry and in making chlorin.

Manganese acts as a base-forming element forming chlorids, sulfates, and nitrates. It also acts as an acid-forming element in the manganates and permanganates. Potassium permanganate is a crystalline solid used as an antiseptic, a disinfectant, and a bleaching agent.

As a base-forming element chromium forms chromous and chromic salts. It acts as an acid-forming element in the chromates and di-chromates. Potassium di-chromate is used in making leather; it is also used in photogravure and half-tone work. Chromium compounds are also used as pigments and mordants.

## **QUESTIONS AND PROBLEMS**

- 1. What purpose does spiegeleisen serve in making steel?
- 2. Would the change of a chromate to a di-chromate be one of oxidation, reduction, or neither?
- 3. What would be the effect of adding a solution of potassium permanganate to a ferrous solution?
- 4. In voltaic cells the accumulation of hydrogen at the positive plate weakens the voltage. What would be the effect of adding manganese dioxid to such a cell?

## CHAPTER XXXIX

## PLATINUM AND OTHER METALS

422. Platinum.—Platinum occurs native, the Ural Mountains producing the bulk of the world's supply. It is a soft, white metal. Its specific weight is 21.4, it being one of the heaviest metals known. It is very ductile and malleable.

Platinum is not affected by air, nor does it oxidize when heated. It has a high melting point, about 1780°C. No single acid affects it, but aqua regia acts upon it slowly. Fused alkalis attack it quite readily. It forms alloys with several metals. For this reason salts of easily reducible metals like silver and lead should not be heated in platinum ware.

- 423. Uses.—Since platinum is not easily melted and few chemicals attack it readily, it is used for making such laboratory utensils as crucibles, dishes, forceps, etc. Platinum wire and foil find use in all chemical laboratories. As a catalytic agent platinum is important, especially in the manufacture of sulfuric acid. Platinum is also used in jewelry. Its salts are used in photography. The demand for this metal exceeds the supply and the price is constantly increasing. At present (1918) it is worth about \$110 per troy ounce.
- 424. Iridium resembles platinum to some extent. An alloy of platinum and iridium is used for standard weights and measures. Gold pens are often alloyed with iridium.
- 425. Tungsten is a white metal that finds use in making self-tempering steels. Its melting point is so high, about

3000°C., that it makes an excellent material for making the filaments for incandescent electric lamps. At first the tungsten filaments were molded and were quite brittle, but a method of drawing tungsten into fine wires has recently been perfected. These wires are quite tenacious. Tungsten lamps use about two-fifths as much current as the old carbon-filament lamps. Tungsten is replacing platinum to a considerable extent for electrical contacts, X-ray bulbs, and in electric resistance furnaces. Sodium tungstate is used for fireproofing cloth.

- 426. Molybdenum also has a very high melting point. It is used for making a type of electric furnace used by dentists. Some of its compounds are used in analytical chemistry.
- 427. Vanadium and Titanium are used in special steels. Titanium serves as a purifier of steel and also increases its wearing capacity.
- 428. Selenium is an element belonging to the sulfur group. It is a non-conductor of electricity in the dark, but it becomes a fair conductor when exposed to the light. It is used in several automatic electrical devices, such as fire-alarms and burglar-alarms. A method of transmitting photographs by electricity based upon this varying resistance of selenium has been fairly successful.
- 429. Thorium and Cerium are extracted from monazite sands. Gas mantles are made by knitting China grass into the desired shape, dipping it into a mixture of the nitrates of cerium and thorium and then igniting the whole to convert the nitrates into the oxids of these elements. It was found that a mixture containing 99 per cent. thorium oxid and 1 per cent. cerium oxid is the most efficient.

### **OUESTIONS**

1. Summarize the properties of platinum that make it suitable for use in making laboratory utensils.

- 2. In what respects is platinum better than gold for use in making laboratory crucibles?
- 3. Would you use a platinum or a silver dish in which to melt sodium hydroxid? Why?
- 4. Why does platinum occur chiefly in the uncombined state in nature?
- 5. What properties has tungsten that fit it to replace platinum in electrical contacts?

## CHAPTER XL

## RADIUM AND RADIO-ACTIVE ELEMENTS

- 430. Uranium.—This element is found in the mineral pitchblende. It finds some use in producing greenish-yellow fluorescent glass, while some of its compounds are used in analytical work in chemistry.
- 431. Radio-activity.—In 1896 Henri Becquerel, a Frenchman, discovered that uranium affects a photographic plate





Fig. 125.—Radiographs. The cut at the left was made by the action of radium rays. The one at the right by the X-rays. (Courtesy of Radium Limited U. S. A.)

in the dark. The action also takes place when the plate is wrapped in a sheet of opaque paper. These radiations emitted by uranium act in these respects very much like the X-rays in their ability to penetrate opaque substances. Substances like uranium that give off radiations of this nature are said to be radio-active (Fig. 125).

432. Discovery of Radium.—Soon after this discovery of Becquerel, M. and Mme. Curie began a series of investigations to determine whether other elements show radioactivity. Thorium was found to be active and Mme. Curie also discovered that pitchblende, the mineral from which uranium is obtained, is several times as active as uranium itself. She concluded that this mineral must therefore contain some other element far more active than uranium. She patiently worked over several tons of pitchblende and succeeded in extracting a few milligrams of the chlorid of an element more than 1,000,000 times as active as uranium. She named this element radium. Radium is usually used in the form of its chlorid, bromid, or carbonate. Mme. Curie succeeded, several years later, in 1910, in isolating metallic radium. Chemically it resembles barium,

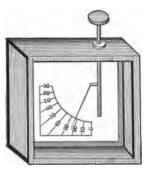


Fig. 126.—An electroscope.

and its salts have properties similar to the salts of barium. The metal and its salts are radioactive.

433. Radium.—This element is a very remarkable one, as the following list of unusual properties clearly shows: (1) It affects a photographic plate, even through opaque substances like paper, etc. (2) Radium compounds discharge an electroscope

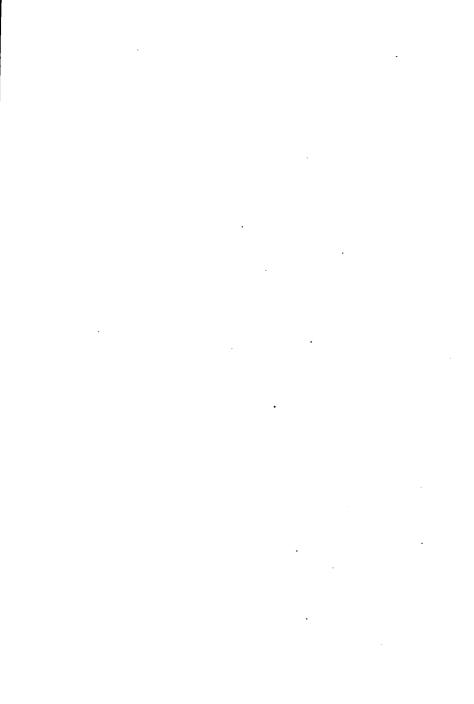
(Fig. 126) since they are capable of ionizing the air and thus making it a conductor of electricity. (3) Radium produces fluorescence when its rays act upon some other chemicals, such as zinc sulfid. (4) It is chemically active, decomposing water, changing oxygen into ozone, imparting a purple color to glass, etc. (5) It acts physiologically producing severe burns and even killing small animals. Many investigators have suffered severe burns that re-



Marie Slodowska Curie (1867----) was born in Poland. After Henri Becquerel discovered the radioactivity of uranium, M.Curie in collaboration with her husband, Pierre Curie, examined other substances in an effort to learn whether they are radio-active. From pitch-blende she isolated radium. She also discovered polonium, another very active element. In 1903 M. and Mme. Curie shared the Nobel prize with Becquerel. She is now professor of physics at the Sorbonne.

Michael Faraday (1791-1867) was a very distinguished English physicist and chemist. While apprenticed to a book-binder he heard Sir Humphrey Davy lecture and wrote him, expressing a desire to be employed in some intellectual pursuit. He studied under Sir Humphrey Davy. He believed that gases are liquids with a low boiling point, and succeeded in liquefying several of them. In chemistry he discovered benzol. In physics he is known for his laws of electrolysis and his studies in electro-magnetic induction leading to the dynamo.





quire a long time to heal as a result of working with this element. It destroys the germinating power of seeds. It destroys bacteria. (6) Radium glows in the dark, the chlorid producing a pale light similar to a phosphorescent glow. (7) It gives off enough heat every hour to more than melt its own weight of ice.

Since radium and its compounds give off heat and light constantly without apparent loss of weight, it was at first believed that they do not conform to the law of the conservation of energy. More recent investigations show that they do not give off heat and light indefinitely, but that radium compounds lose one-half their activity and energy in about 1700 years, one-half of what remains in the next 1700 years and so on.

434. Disintegration of the Atom.—Following the discovery of radium the question arose, "What is the source of this energy that is liberated?" A great deal of work has been done in studying this fascinating element, and it has been quite conclusively proven that the energy of radioactive substances is sub-atomic. The atoms of such elements explode or disintegrate spontaneously. The radium atom is heavy, its atomic weight being 226. As it decomposes two other elements are formed, helium, having an atomic weight of 4, and niton, having an atomic weight of 222. The heating effects produced by radio-active substances are evidently due to collisions between the particles emitted as the explosion occurs. Thus we see also that it is actually possible for one element to break up and form other elements by transmutation. Niton, or radium emanation, also breaks up forming radium A, an element having the atomic weight 218. Radium A disintegrates forming successively, Radium B, C, D, E, and F. When radium F breaks up it forms an element whose atomic weight is 206. It is believed to be lead. If this is true, lead is the final disintegration product of radium.

- 435. Nature of the Becquerel Rays.—The radiations from such substances as radium, thorium, and uranium are called Becquerel rays. Their nature was carefully studied by Rutherford, who found that they are complex, consisting of three different classes:
- 1. The  $\alpha$ -rays, or alpha rays, are identical with positively charged helium particles. They are shot out from the disintegrating atom with a velocity of 10,000 to 20,000 miles per second. Their penetrating power is not so great as that of the other rays, a thin sheet of aluminum foil being sufficient to intercept them; but their heating effect as well as their ability to ionize air-molecules is much greater. Severe radium burns are largely due to the alpha rays.
- 2. The  $\beta$ -rays, or beta rays, are negatively charged particles about  $\frac{1}{2000}$  as heavy as the hydrogen atom. Their velocity is from 60,000 to 160,000 miles per second, hence they have a greater penetrating power than the alpha particles.
- 3. The  $\gamma$ -rays, or gamma rays, appear to be of the same nature as the X-rays. They have greater penetrating power than either the alpha or the beta particles. They are probably not particles at all, but pulses set up in the ether by the bombardment of the other particles.
- 436. Uses of Radium.—Since radio-active compounds destroy bacteria radium was at first heralded as a cure-all. Several attempts have been made to use it in curing such diseases as cancer, lupus, and scrofula. In some cases the treatment appears to have been very successful, while in other cases it has been a total failure. Two factors have been militant against its extensive use: (1) Radium is very expensive, the chlorid costing about \$100 per milligram, or nearly \$2,000,000 per ounce. (2) The frightful burns that it produces when improperly used make its use quite limited. It is still too early to determine whether its use in medicine is likely to become reasonably successful.

Radium and other radio-active compounds are being quite extensively used to make luminous paint.

437. Effect of the Discovery of Radium on Chemical Theory.—We have already seen that it at first appeared as if radium and similar substances do not conform to the law of the conservation of energy. This apparent discrepancy is explained when we know that the average life of a radium atom is about 2500 years, and that as it explodes or disintegrates the emitted particles collide with each other and with surrounding molecules, producing heat energy.

Our conception of the atomic theory, however, must be somewhat modified. The atomic theory assumes that atoms are indivisible, but in the case of radio-active elements we find that the atoms slowly disintegrate, forming helium atoms, and emitting negatively charged particles to which the name electron has been given. J. J. Thomson, the scientist who developed the electron theory of matter considers that the atom is not the simple substance it was once thought to be, but that it is made up of a positive nucleus surrounded by a large number of electrons. This new theory does not materially affect practical chemistry since neither heat, cold, light, nor electricity affects the rate of decomposition of radio-active elements. The action is entirely spontaneous and so far no one has been able to accelerate or retard it. Thomson estimates that the stored energy in 1 gram of hydrogen amounts to  $6 \times 10^{11}$  footpounds. Whether man will ever find a way to unlock the enormous energy stored in atoms and put it to practical use is uncertain, but it furnishes an interesting problem for future investigators.

The old alchemists believed it was possible to transmute one element into another. They spent much time in looking for the "philosopher's stone," which they believed would change the base metals, lead, iron, copper, etc., into gold. Chemists scoffed at these views of transmutation,

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but now we have at least three elements that spontaneously decompose forming other elements by transmutation. It is quite certain that elements having lower atomic weights, as iron and copper, can not form gold or silver by transmutation, yet it is equally certain that elements having very high atomic weights can and do form simpler atoms by disintegration.

Topics for Reference.—Discovery of radium. Age of the earth from atomic disintegration. Radium cures.

### CHAPTER XLI

# CHEMISTRY OF THE COMPOUNDS OF CARBON

- 438. Introductory.—The compounds formed by plants and animals were formerly included in organic chemistry, since it was believed that some living organism was needed to produce them. This name is still used for such compounds, elementary carbon and the carbonates usually being included with inorganic substances. In 1828 Wohler, a German chemist, prepared urea by synthesis. Since that date a large number of the compounds formerly obtained from plants and animals have been made in the laboratory. Since all these compounds contain carbon, "the chemistry of the compounds of carbon" seems to be a more fitting name for this division of chemistry.
- 439. Source of Carbon Compounds.—We have already learned that certain hydrocarbons and some other carbon compounds are obtained by the destructive distillation of wood and soft coal. Many hydrocarbons are obtained from petroleum and coal-tar. Alcohol is obtained by the fermentation of fruits and grains. The fruits also yield organic acids and sugar. Starch is made from the cereals, while fats and oils are obtained from animals, nuts, and seeds. Cellulose comes from cotton and various other vegetable fibers.
- 440. Petroleum.—Petroleum is a thick liquid, often of a greenish-black color, that is obtained from the earth's crust. It may be found near the surface or at a depth of 2000 or more feet. Holes about 6 to 8 in. in diameter are drilled in the earth until the oil stream or reservoir is reached (see Fig. 127). If considerable natural gas is

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present, the oil is forced out forming what is called a "gusher" (Fig. 128). Some wells of this kind flow several

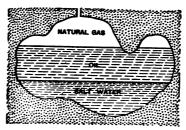


Fig 127.—Possible condition of an underground oil reservoir.



Fig. 128.-A gusher.

hundred barrels of oil per day. The oil may rise to a point near the surface from which it is pumped into storage tanks. The crude oil is then pumped through pipe lines

to the refineries, sometimes for a distance of 1500 miles (Fig. 129).

441. Refining Petroleum.—Petroleum is a mixture of several hydrocarbons, of which petroleum ether, gasoline, naphtha, benzine, kerosene, gas oils, lubricating oils.



Fig. 129.—General view of oil field, showing derricks and temporary storage tanks.

vaseline, and paraffin are the most important. They may be separated from one another by fractional distillation. Fig. 130 shows the method of separating petroleum into several distillates by fractional distillation. From these distillates many products are obtained by further fractionation. To increase the yield of gasoline the oils are superheated to produce "cracking." In purifying these oils they are washed with sulfuric acid, an alkali, and water in turn.

442. Uses of Petroleum Products.—Petroleum ether is used as a solvent. Gasoline, naphtha, and benzine are used as solvents; they are also extensively used as fuels, especially in internal-combustion engines. Benzine is

sometimes used as a substitute for turpentine. Kerosene serves as a fuel and is used for illuminating purposes. It should have a flash-point of at least 110°F. to make it safe for use in lamps. Vaseline serves as an ointment and as a lubricant for use as cup-grease and axle-grease. Paraffin is used in making candles and chewing gum; it also finds use for insulating electrical apparatus and in water-proofing paper and fabrics. Crude oil is used as a fuel on some battleships.

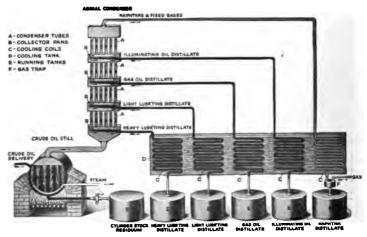


Fig. 130.—Fractional distillation of crude petroleum. (Courtesy of Platt & Washburn Refining Company.)

### HYDROCARBONS

443. Hydrocarbons.—A hydrocarbon is a compound of hydrogen and carbon. Since the valence of carbon is 4, we might expect that CH<sub>4</sub> would be the only compound of these two elements. As a matter of fact more than 200 hydrocarbons are known. Such a large number is possible since one carbon atom has the rather unusual ability of combining with other carbon atoms, as the following structural formulas show:

If we examine these formulas we will observe that each one differs from the preceding one by the group,  $CH_2$ . A series of compounds each differing from the preceding by such a group, or homolog, is known as an homologous series. The homolog,  $CH_2$ , is very common in organic chemistry. These compounds form the first four of the paraffin series, or the methane series. The following table gives a few of the 60 known representatives of this series.

Name	Common name	Formula CH4	Melting point	Boiling point	
Methane					−164°C.
Ethane		C <sub>2</sub> H <sub>6</sub>		Gases	−90°C.
Propane		C <sub>8</sub> H <sub>8</sub>		C. C	−37°C.
Butane		C4H10			1°C.
Pentane	A mixture of pentane and hexane forms pe- troleum ether	C <sub>5</sub> H <sub>12</sub>			36°C.
Hexane	A mixture of hexane and heptane forms gasoline	C6H14			71°C.
Heptane	-	C7H16		Liquids	98°C.
Octane	A mixture of octane and nonane forms benzine	C8H18			125°C.
Nonane		C0H20	l l		150°C.
Decane	A mixture of hydro- carbons from decane to hexadecane is kerosene	C10H22		l	173°C.
Hexadecane		C16H24	18°C.		288°C.
		C60H122	102°C.	Solids {	

A study of the above table shows that the melting points and the boiling points of these hydrocarbons rise as the molecular weight increases. It is not necessary to memorize the formulas since the number of hydrogen atoms in the compound can be obtained by multiplying the number of carbon atoms by two and adding two to the product. Thus the general formula for hydrocarbons of this series is  $C_nH_{2n+2}$ 

444. Methane.—CH<sub>4</sub>. This gas is formed in nature by a decomposition of organic compounds. It forms about 90 per cent. of natural gas. It is liberated when the mud at the bottom of stagnant pools of water is stirred, hence the name marsh gas. It is frequently found in coal-mines and called by the miners fire-damp. It may be made in the laboratory by the action of aluminum carbid on water:

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4.$$

Methane burns with a pale yellow flame. It is used as a fuel.

445. Ethylene, C<sub>2</sub>H<sub>4</sub>, is the first member of a second series of hydrocarbons. Its structural formula is

$$H$$
  $C = C$   $H$ 

An organic compound having a double bond between two carbon atoms is said to be *unsaturated*, since other elements may be added to it directly to form new compounds. For example,

$$\begin{array}{c} H \\ H \\ \end{array} = C \\ \begin{array}{c} H \\ H \\ \end{array} + Cl_2 \rightarrow \begin{array}{c} Cl \\ H \\ H \\ \end{array} \\ C - C \\ \begin{array}{c} Cl \\ H \\ \end{array}$$

Ethylene is a gas that burns with a bright flame. It finds use as an illuminant.

- 446. Acetylene,  $C_2H_2$ , is the most important member of a third series of hydrocarbons. Its preparation, properties, and uses have already been discussed. It is also an unsaturated hydrocarbon as its structural formula,  $H C \equiv C H$ , shows.
- 447. Benzol.—C<sub>0</sub>H<sub>6</sub>. Benzol, or benzene, is a polymer of acetylene, having the same percentage composition, but a different formula and a greater molecular weight. Benzol can be formed when acetylene is passed through hot tube:

$$3C_2H_2 \rightarrow C_6H_6$$
.

Benzol is a colorless liquid obtained from the distillation of coal-tar. It is the simplest compound in the aromatic series of hydrocarbons:

benzol, 
$$C_6H_6$$
.  
toluol,  $C_7H_8$ .  
xylol,  $C_8H_{10}$ .

All of these compounds find extensive use in the manufacture of dye-stuffs. They are good solvents; toluol also finds use in making explosives. The following structural formulas are generally accepted as being the correct formulas for benzol and toluol:

448. Other Hydrocarbons.—Naphthalene, C<sub>10</sub>H<sub>8</sub>, is a coal-tar compound. It crystallizes in white shining scales. It is used in "moth-balls" and in the manufacture of drugs

and dye-stuffs. Anthracene,  $C_{14}H_{10}$ , is also obtained from coal-tar. It is used in the preparation of alizarin, a red dye. Turpentine,  $C_{10}H_{16}$ , is a hydrocarbon obtained from the long-leaved pine. It is used medicinally and also in the paint and varnish industry. Asphalt consists chiefly of a natural mixture of hydrocarbons. The island of Trinidad furnishes large quantities of asphalt, which is used for paving streets.

## SUBSTITUTION PRODUCTS OF THE HYDROCARBONS

449. Preparation.—Substitution products of the hydrocarbons are prepared by replacing one or more of their hydrogen atoms with elements like the halogens, or with such groups as OH, NO<sub>2</sub>, etc. For example, mono-chlormethane, CH<sub>3</sub>Cl, may be made by treating methane with chlorin:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl.$$

By further treatment with chlorin, other hydrogen atoms are replaced in turn, resulting in the formation of such compounds as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub>.

- 450. Chloroform.—CHCl<sub>3</sub>. Although chloroform is a substitution product of methane and could be made by the action of chlorin on this gas, yet it is cheaper and far more convenient to make it by the action of chlorin on alcohol when an alkali is present. Chloroform is a heavy, oily liquid. It has a sweet, rather pleasing odor. Its vapor produces insensibility to pain when inhaled, hence chloroform is used as an anesthetic. It finds some use as a solvent.
- 451. Iodoform.—CHI<sub>3</sub>. Like chloroform, iodoform is also made from alcohol. It is a yellow crystalline solid, having a very persistent odor. It is used chiefly as an antiseptic surgical dressing.

- 452. Carbon Tetrachlorid.—CCl<sub>4</sub>. This compound is a colorless compound somewhat resembling chloroform. It is used extensively as a solvent. For removing grease spots and other stains it is quite as good as gasoline, and its vapor is not explosive. "Carbona," a cleansing fluid, contains carbon tetrachlorid. It is also used in some small fire extinguishers; for example, "Pyrene."
- 453. Nitro-benzol.—C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>. If benzol is treated with nitric acid in the presence of sulfuric, a heavy oily liquid known as nitro-benzol is formed, the NO<sub>2</sub> group being substituted for one of the hydrogen atoms of the benzol. It is used extensively in the manufacture of aniline.
- 454. Aniline.— $C_6H_5NH_2$ . Aniline formerly came from the anil plant but it is now generally made by treating nitro-benzol with nascent hydrogen. Enormous quantities are used in the dye industry. Toluidine and xylidine, compounds made from toluol and xylol respectively in a manner analogous to the making of aniline, are also used in the dye industry. When we stop to consider that benzol, toluol, xylol, naphthalene, and anthracene are all coal-tar compounds, we can readily understand why this tarry mixture is so important in the dye industry.

### **ALCOHOLS**

455. Alcohols.—The alcohols all have one or more OH groups. Although they can be formed indirectly from the hydrocarbons, they are more often prepared by other methods. For example, wood alcohol is made by the dry distillation of wood; it is called *methyl alcohol* since it differs from methane only in the fact that an OH group has been substituted for one of the hydrogen atoms of that gas. The CH<sub>3</sub> group acts like a radical and is given the name *methyl*. If we treat mono-chlor-methane, or methyl chlorid, with potasssium hydroxid wood alcohol is formed:

 $CH_{3}Cl + KOH \rightarrow CH_{3}OH + KCl.$ 

A large number of alcohols are known but wood alcohol and grain alcohol are the most important.

- 456. Wood Alcohol.—CH<sub>2</sub>OH. Commercially wood alcohol is obtained by the destructive distillation of wood. When pure it has rather a pleasant odor, but the commercial product contains impurities that impart to it a disagreeable odor. It is a light liquid, boiling at 66.7°C. It is very poisonous; cases of poisoning from wood alcohol even when used externally are not uncommon. Its vapor attacks the eyes. When taken internally or inhaled, it often affects the optic nerve, producing partial or total blindness. It is a good fuel, since it burns with a hot smokeless flame. It also finds use as a solvent of oils, resins, and shellac.
- 457. Fermentation.—If we add a little yeast to a dilute water solution of sugar or molasses, chemical action soon takes place. Bubbles of gas, which are found to be carbon dioxid, are liberated and alcohol is formed in the solution:

$$\uparrow C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2.$$

Any chemical change that is brought about by the action of some organic body, or ferment, is known as fermentation. The organic body in the above example is an enzyme secreted by the yeast plants. The enzyme acts like a catalytic agent in changing the sugar into alcohol and carbon dioxid. This type of fermentation, in which alcohol is formed, is known as vinous fermentation. There are many types of fermentation, certain kinds of bacteria being active in producing the chemical change. Thus the making of vinegar, the souring of milk, the formation of rancid butter, and the decay of foods are all examples of fermentation caused by plant organisms.

458. Grain Alcohol.—C<sub>2</sub>H<sub>5</sub>OH. We have seen that ordinary alcohol can be produced by the action of an enzyme on fruit juices or dilute sugar solutions. On a large scale

it is prepared by the fermentation of such starchy grains as barley, rye, and corn. These grains are first sprouted to change the starch to sugar, this change being produced by the ferment diastase. They are then crushed and treated with water and yeast to produce alcoholic fermentation.

Beer, claret, ale, hard cider, and the various wines are all beverages that are produced by fermentation of fruits or grains. They are known as fermented liquors. When the per cent. of alcohol in a fermented liquor amounts to about 14 per cent., fermentation stops, since alcohol of this strength renders the ferment inactive. Stronger liquors are made by distillation or by fortifying fermented liquors by the addition of alcohol.

In producing a distilled liquor some fermented liquor, which we have seen contains not more than 14 per cent. of alcohol, is heated until the boiling point of alcohol (78°C.) is reached. The mixture is boiled until all the alcohol is driven off, but the distillate that condenses contains some water, as water evaporates quite rapidly at 78°C. The per cent. of alcohol is, however, much higher than that of the original mixture. By re-distilling this distillate, the per cent. of alcohol is increased still more. Whiskey, brandy, gin, and rum are distilled liquors containing from 50 to 80 per cent. alcohol.

A liquid containing more than 95.5 per cent. alcohol can not be obtained by fractional distillation, since a mixture containing 95.5 per cent. alcohol and 4.5 per cent. water boils at a slightly lower temperature than pure alcohol, and distils as a uniform mixture. Ordinary alcohol is 95 per cent. alcohol. The last traces of water may be removed from alcohol by adding to it some dehydrating agent; generally lime is used. Absolute alcohol is water free, or nearly 100 per cent. pure.

Since grain alcohol is really a substitution product of ethane, its chemical name is ethyl alcohol. It is a colorless

liquid, having a peculiar odor and a sharp, biting taste. It has a strong affinity for water and mixes with it in all proportions. It is not so poisonous as wood alcohol, but when taken internally it produces intoxication. During the first stages, it causes the blood to flow to the surface, thus producing a feeling of warmth and vigor that has led to the popular idea that alcohol is a stimulant. Later the heart action becomes slower and the temperature falls below normal, showing that alcohol is really a narcotic. Alcohol burns with a nearly colorless blue flame.

In addition to the use of alcohol as a beverage, it finds some use as a fuel. It is an excellent solvent of resins and is used in the varnish industry. In pharmacy it is used for extracting from plants their medicinal constituents. Thus such substances as bay rum and witch hazel extract contain from 15 to 20 per cent. alcohol. *Tincture of iodin* contains 5 per cent. of iodin dissolved in alcohol. Lemon extract should contain not less than 5 per cent. lemon oil. To dissolve this oil alcohol of about 80 per cent. strength is needed. Vanilla extract is made from resins of the vanilla bean dissolved in 50 per cent. alcohol.

459. Denatured Alcohol.—Prior to 1907 an internal revenue tax of about \$2.00 per gallon had been levied on all alcohol made in the United States, whether it was to be used for industrial purposes or as a beverage. Since manufacturers in this country who used considerable quantities of alcohol could not compete with foreign manufacturers who had no tax to pay, Congress in 1906 passed a law making alcohol which is to be used for industrial purposes exempt from taxation, provided it is properly "denatured." Grain alcohol is "denatured" by mixing with 90 to 95 parts, from  $4\frac{1}{2}$  to 10 parts of wood alcohol and  $\frac{1}{2}$  part of benzol. The addition of these substances renders it unfit to be used as a beverage but does not interfere with its use in the industries and arts.

- 460. Glycerol.—C<sub>3</sub>H<sub>5</sub>(OH)<sub>8</sub>. Glycerin, or glycerol; is a tri-acid alcohol. It is a thick viscid liquid, colorless and odorless, but having a sweet taste. Its most important use is in the manufacture of nitroglycerin. It is also used in some toilet soaps, and medicinally in various lotions.
- 461. Phenol.—C<sub>6</sub>H<sub>5</sub>OH. Chemically phenol is an alcohol obtained from coal-tar, but since it has very feeble acid properties it is commonly known as carbolic acid. It is closely related to benzol, as its formula indicates. Pure phenol forms colorless crystals, having a peculiar, persistent odor. It is used in making picric acid for explosives and as a disinfectant. Recently it is being used with formaldehyd to form such substances as bakelite and condensite which are used for insulating materials, phonograph discs, etc.

The *cresols* are hydroxids of toluol that find extensive use in preserving wood. They are excellent disinfectants.

#### ETHER

462. Ether.— $(C_2H_5)_2O$ . Ether is formed by heating alcohol with sulfuric acid at the proper temperature. Ethers are organic oxids. Ordinary ether, or ethyl ether, is a light mobile liquid boiling at about 35°C. It is used to some extent as a solvent, but more extensively as an anesthetic. Nitrated cellulose forms in ether a colloidal suspension. From the jelly-like mass smokeless powder is formed.

#### **ALDEHYDS**

**463.** Formaldehyd.— $H \cdot CHO$ . Aldehyds are prepared by the partial oxidation of alcohols. Formaldehyd, the most important of this group of compounds, is prepared by partially oxidizing wood alcohol:

$$CH_3OH + O \rightarrow H \cdot CHO + H_2O.$$

This aldehyd is a gas at temperatures above 21°C. It is sold under the name *formalin*, which is a 40 per cent. water solution of the gas. It is one of the best disinfectants known. Formalin is often used on seeds before planting to destroy injurious fungi. Potatoes so treated are less apt to be affected by scab. It also finds use in preserving anatomical specimens, and illegally as a food preservative.

Benzaldehyd, C<sub>6</sub>H<sub>5</sub>·CHO, is found in almonds and in cherry kernels. It is used as a flavor. Vanillin, C<sub>7</sub>H<sub>7</sub>·CHO, is an aldehyd extracted from the vanilla bean, or it may be prepared artificially. It is used as a flavor in vanilla.

### ORGANIC ACIDS

464. Acids.—If we oxidize the aldehyd studied in the last paragraph, an organic acid is formed:

$$H \cdot CHO + O \rightarrow H \cdot COOH$$
.

All organic acids have one or more carboxyl (COOH) groups. A very large number are known, some of them being quite important compounds. While they can be made by the oxidation of their corresponding alcohol or aldehyd, the majority of them are obtained from their salts found in plants. Some of them are produced by fermentation.

- 465. Formic Acid.—H · COOH. This acid stands first in an homologous series of organic acids related to the paraffin series of hydrocarbons. It is found in nature in red ants, in some bee stings, and in stinging nettles. Although a weak acid chemically, yet physiologically it is active enough to blister the skin. Its salts, known as formates, are used as mordants.
- 466. Acetic Acid.—CH<sub>3</sub> · COOH. This acid is obtained by the destructive distillation of wood. It is also formed by the action (on alcohol) of a ferment known as "mother

of vinegar." In this manner the alcohol in hard cider is slowly changed to acetic acid:

$$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O.$$

Acetic acid containing less than 0.5 per cent. water crystallizes at a temperature of 16°C. forming glacial acetic acid. This acid is a good solvent of organic substances. Its salts known as acetates have the (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) radical; they are used as mordants.

Acetic acid is the active substance found in vinegar, it being present to the extent of from 4 to 6 per cent. Natural vinegar is made by two successive fermentations of the juices of fruits, usually from the juice of apples. Artificial vinegar is made by the oxidation of alcohol.

- 467. Oxalic Acid.—(COOH)<sub>2</sub>. Oxalic acid is a white crystalline solid. Since it has two carboxyl groups, it is a di-basic acid. Its salts, the oxalates, are found in several plants, such as rhubarb, oxalis, and other sorrels. It is an active poison. Oxalic acid finds use in calico printing, as a reducing agent, in bleaching flax and straw, and in cleaning brass and copper.
- 468. Tartaric Acid.—(CHOH)<sub>2</sub>(COOH)<sub>2</sub>. When grape juice ferments, "tartar," or impure acid potassium tartrate, is deposited in the form of crystals, since it is insoluble in alcohol. From this "tartar" the acid may be obtained. Acid potassium tartrate,  $HK(C_4H_4O_6)$ , is cream of tartar. Both the acid and this salt are used in baking powder. Sodium potassium tartrate is known as Rochelle salts.

in lemons and other citrous fruits. It also occurs in raspberries, gooseberries, and currants. Its magnesium salt is used in medicine.

# ETHEREAL SALTS OR ESTERS

- 470. Occurrence.—Many esters are found in nature in fats and oils, as well as in certain volatile oils that give to plants and their fruits their odor and flavor. Since many of them have a pleasant odor, the name ethereal salts is often given to this class of compounds. For example, oil of wintergreen is a salt of wood alcohol and salicylic acid known as methyl salicylate. Banana oil, which is used in aluminum paint, is amyl acetate. An ethereal salt of ethyl alcohol and butyric acid has the flavor of pineapple extract. This is rather interesting when we consider that butyric acid is present in rancid butter.
- 471. Preparation of Esters.—Esters may be prepared by the action of an alcohol on an organic acid. For example,

$$\begin{array}{c} C_2H_5OH \ + \ CH_3COOH \ \rightarrow \ C_2H_5 \cdot C_2H_3O_2 \ + \ H_2O. \\ \text{Ethyl alcohol} \ + \ \text{Acetic acid} \ \rightarrow \ \ \text{Ethyl acetate} \ \ + \ \ \text{Water} \end{array}$$

The alcohol acts like a base in neutralizing the acid to form an ethereal salt. Since many esters are salts of very weak acids and very weak bases they hydrolyze readily. For this reason the above reaction is reversible unless some dehydrating agent like sulfuric acid is present to take up the water that is formed. Esters are also formed when an alcohol is acted upon by an inorganic acid. Thus we have seen that nitric acid acts upon glycerol to form glyceryl nitrate, or nitro-glycerin, an ethereal salt.

472. Saponification.—Many of the common fats and oils are glyceryl salts of such organic acids as stearic, palmitic, and oleic. They are ethereal salts, or esters. Stearin, the glyceryl salt of stearic acid forms the chief constituent of beef and mutton tallow. Palmitin is a salt of palmitic acid found in palm oil. Olein is a salt of oleic acid that forms a considerable proportion of lard, olive oil, and cottonseed oil. When these fats or oils are treated

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with a strong base like sodium hydroxid, the sodium salt of these acids, or *soap*, is formed and *glycerol* is obtained as a by-product:

 $C_3H_5(C_{17}H_{35}CO_2)_3+3NaOH\rightarrow 3NaC_{17}H_{35}CO_2+C_3H_5(OH)_3$ Glyceryl stearate + Sodium hydroxid  $\rightarrow$  Sodium stearate + Glycerol

Saponification may be defined as the process of converting fats or oils into soap by treating them with a strong base. More

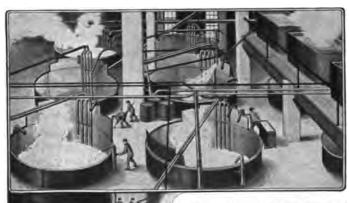


Fig. 131.—Kettles in which soap is boiled. The largest kettles are 50 feet deep and about 20 feet in diameter. They hold about 1,000,000 pounds apiece.

broadly, it includes the hydrolysis of all esters. Soap is usually a mixture of the sodium salts of the organic acids mentioned above. For example Castile

above. For example, Castile

soap is sodium oleate made by boiling a low-grade olive oil with sodium hydroxid (Fig. 131). Soft soaps and liquid soaps are usually made by using some potassium hydroxid in saponification. Shaving soaps are often mixed sodium and

potassium salts of the above acids. When soap is added to hard waters the sodium and potassium salts, which are soluble, unite with the calcium and magnesium salts in the hard water to form "lime soap" or "magnesium soap." Both of these compounds are insoluble, and no suds can be produced until enough soap has been added to precipitate them completely. A soap that will lather in sea-water, known as marine soap, is made from cocoanut oil. It contains a high per cent. of water.

473. Fillers and Adulterants.—In the manufacture of soap some water is incorporated with it. The soap is then dried to give it the proper hardness and prevent its dissolving too rapidly. A hard soap should not contain more than 25 per cent. of water. Rosin is nearly always added to a laundry soap since it increases its lathering power. As it aids in the cleaning process, rosin should be classed as a filler rather than as an adulterant. Sodium silicate is added as a filler in some soaps. Its cleansing properties are slight, and it is injurious to certain fabrics, hence it is usually classed as an adulterant. A laundry soap usually contains a slight excess of the base to aid in removing grease or oil from the fabrics. A toilet soap should not contain free alkali as it will cause the skin to chap or crack.

474. Cleaning and Laundering.—Dirt may usually be readily removed from the clothing by the mechanical action of water unless grease or oil is present. In such a case the grease sticks to the fiber and the dirt which adheres to it can not be removed since the binding material is insoluble in water. Soap is water-soluble and it owes its cleansing power to its ability to form an emulsion with fats and oils. The minute fat globules which are held in suspension by the soap solution are easily carried away by the agitation of the water.

Wool and silk are usually "dry cleaned," since they are

apt to be injured by the action of soap and water. In the "dry cleaning" process some substance like gasoline, benzol, or carbon tetrachlorid, is used to dissolve the grease. It may then be absorbed by the use of blotting paper, or with such powders as French chalk or fuller's earth. Carbon tetrachlorid is one of the safest solvents to use since its vapor does not form explosive mixtures with air.

475. Special Soaps and Scouring Powders.—The floating soaps are made by beating air into the soap while it is still liquid. Transparent soaps frequently contain glycerin. They may also be made by dissolving the soap in alcohol. Dyes and perfumes are generally added to toilet soaps. The various medicated soaps are made by adding to them some substance of supposed medicinal value. Powdered soaps are made by grinding a dry, hard soap to a fine powder. If such a soap is to be used in the laundry, sodium carbonate is usually added. Naphtha soaps contain a small per cent. of naphtha.

Scouring powders are generally mixtures of powdered soap, sodium carbonate, and such gritty substances as powdered sand or pumice stone. Many of them contain from 80 to 90 per cent. of insoluble matter.

476. Butter—Oleomargarine.—Butter is an animal fat obtained from milk. The federal law requires that butter shall contain at least 82.5 per cent. fat and not more than 16 per cent. water. These fats are mainly olein, stearin, and palmitin, but the flavor of butter is largely due to an ester of butyric acid and the presence of small quantities of ethereal salts of capric, caproic, and caprylic acids. Certain bacteria cause butter to ferment or become rancid, the disagreeable odor in such event being due to the formation of the acids from the last four esters mentioned. Butyric acid has an unpleasant odor and taste. Capric acid is present in limburger cheese. As these acids are volatile, such butter may be renovated by melting the fat and blowing

air through the molten fat for several hours. Such butter is also called process butter.

Oleomargarine is a butter substitute. It is made from neutral lard, beef fat, cotton-seed oil, and palm oil. It is cheaper than butter and is considered just as nutritious. Few persons can tell the difference between butter and oleomargarine by the taste alone. Nut margarine is made from peanut oil and cocoanut oil.

Butterine is made by adding a certain per cent. of butter to oleomargarine.

## SUMMARY

Organic chemistry is known as the chemistry of the compounds of carbon.

Carbon compounds are obtained by the destructive distillation of wood and coal, from the fractional distillation of petroleum, and from various plants and animals.

A hydrocarbon is a compound containing hydrogen and carbon only. More than 200 are known. They are used extensively as fuels and solvents. Methane, acetylene, benzol, gasoline, kerosene, vaseline, paraffin, naphthalene, and turpentine are all common examples of hydrocarbons.

Certain elements or groups of elements may be substituted for one or more of the hydrogen atoms in a hydrocarbon. Chloroform, iodoform, carbon tetrachlorid, and aniline are important substitution products of hydrocarbons.

Fermentation is a chemical change produced by the action of a living organism or an enzyme.

The alcohols are organic compounds consisting of an organic radical and at least one OH group. Ordinary alcohol is made by the fermentation of sugar. Methyl alcohol, glycerol, and phenol are also important alcohols.

An ether is an oxid of organic radicals. Ethyl ether is the most common, being used as an anesthetic.

Aldehydes have the CHO group. Formaldehyd is the

most common aldehyd. It finds use as a disinfectant and preservative.

Organic acids have the carboxyl (COOH) group. Acetic acid occurs in vinegar. Tartaric acid finds use in baking powder.

Esters are salts of alcohols and acids. They include animal and vegetable fats and oils, fruit flavors, perfumes, nitro-glycerin, etc. Butter and oleomargarine are mixtures of esters or ethereal salts.

Saponification is the process by which fats and oils are converted into soap by boiling them with a strong base.

# QUESTIONS AND PROBLEMS

- 1. What do you understand by an homologous series? Does the relation appear to hold in the same manner in organic acids?
- 2. Why is petroleum such an important substance from an industrial standpoint?
- 3. If you were given a substance containing carbon 92.3 per cent. and hydrogen 7.7 per cent., how could you tell whether it was acetylene or benzol vapor?
- 4. What is the advantage of using structural formulas in organic chemistry?
- 5. At one time coal-tar was thrown away as waste material. Why is it so valuable at the present time?
- 6. Is wood alcohol suitable to use as an alcohol rub? Give reason for your answer.
  - 7. Why is alcohol so important in pharmacy?
- 8. Name one very important part that sulfuric acid plays in organic chemistry. Illustrate, using at least three different cases.
- 9. Would it be possible to produce formic acid by starting with methane? If so, name the different steps in the process.
  - 10. Why does baking soda relieve the pain from bee stings?
- 11. Name some common fillers used in soap. Should they be classed as adulterants?
- 12. Why does not a mixture of gasoline and water make as good a cleansing solution as soap and water?

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- 13. Castile soap is often mottled by putting into it ferrous sulfate. This produces green spots. Why do they become red when exposed to the air?
- 14. State the advantages and disadvantages of using a soap that contains free alkali.

Topics for Reference.—Rittman process. Manufacture of soap. Manufacture of oil-cloth and linoleum.

### CHAPTER XLII

## OTHER CARBON COMPOUNDS

#### **CARBOHYDRATES**

477. Carbohydrates include the various sugars, starch, cellulose, and dextrin. They all contain carbon, hydrogen, and oxygen. In nearly all cases the hydrogen and oxygen are present in the ratio of 2 to 1, the same as in water.

478. Sugars.—Many sugars are known, of which glucose, fructose, maltose, sucrose, and lactose are the most important. Cane-sugar, beet-sugar, and maple-sugar all contain sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>. Cane-sugar is made by squeezing the juice from sugar-cane as the stalks are passed between rollers. It is then clarified by precipitation and by filtering it through bone-black. To avoid scorching the sugar and to facilitate evaporation, the syrup is concentrated in vacuum pans. The student should remember that liquids boil at lower temperatures when the atmospheric pressure is decreased. The "mother liquor" left after the crystals of sugar have been removed is known as molasses. sugar crystals have a natural yellow tint; before sugar is put on the market this yellow tint is neutralized by the addition of some blue pigment, usually ultramarine. Beet-sugar is made from beets in a similar manner. sugar contains some flavoring material that gives it a different taste from beet-sugar and cane-sugar, although it consists largely of sucrose.

When sucrose is heated to 210°C. caramel is formed. This substance is used as a flavoring in candy and ice-cream and as a coloring matter. If we add an acid to sucrose and

heat it to about 70°C. it is converted into two sugars, dextrose and levulose. The process is known as inversion; invert sugar forms a sticky substance instead of crystals. This explains the reason for adding vinegar when making a candy that is to be pulled.

- 479. Milk Sugar.—C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>·H<sub>2</sub>O. Lactose has practically the same composition as cane-sugar. It contains water of crystallization. Lactose is found in milk to the extent of about 5 per cent. Its chief use is as a food and in medicine for coating pills. Certain bacteria present in milk change the lactose by fermentation into lactic acid, which is always present in sour milk.
- 480. Maltose.— $C_{12}H_{22}O_{11}$ . Malt is made by germinating barley in water and then drying it. Barely contains the enzyme diastase, which converts starch into maltose, a very sweet sugar similar to lactose. It is manufactured in large quantities for making alcoholic beverages.
- 481. Dextrose.—C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. This compound is often known as grape-sugar, or sometimes as glucose. It is found in nature in grapes, various other fruits, and honey. Pure grape-sugar is a white crystalline solid about three-fifths as sweet as cane-sugar. We have seen that it is formed by the inversion of sucrose. It is prepared commercially in large quantities by heating starch with hydrochloric acid. Usually dextrose is marketed in the form of glucose, a thick syrupy liquid that contains both dextrose and dextrin. Large quantities of glucose are used in making candies, in molasses, jams, and jellies. It is not injurious, but it forms a highly concentrated food. The only possible objection to its use is when it is sold as a substitute for canesugar at the same price as sugar itself.
- 482. Levulose.—C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. Levulose or fructose is found in many fruits together with glucose. It is formed in equal quantities with glucose during the inversion of cane-sugar. The student will observe that it has the same formula as

dextrose. Two compounds having the same percentage composition and the same molecular weight are said to be isomeric. Dextrose turns the plane of polarized light to the right, while levulose twists this plane to the left. This property furnishes the name for these sugars.

483. Starch.—(C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>. Starch is found in grains, seeds, tubers, and fleshy roots. Most of the starch made in the United States comes from corn, but potato starch is

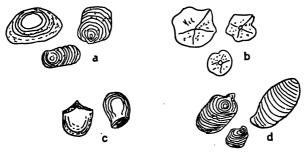


Fig. 132.—Starch grains from various plants.

more common in Europe. Starch is made up of granules that vary in appearance, depending upon the source. By the aid of a compound microscope it is often possible to tell from what plant the starch was obtained (see Fig. 132). Starch is insoluble in water, but when heated the granules swell and burst, and the altered starch forms a colloidal suspension. If only a little water is used a kind of transparent jelly is formed known as starch paste. Starch is used in the laundry in the form of a dilute paste. In the use of cold starch the granules suspended in water are taken up by the fabric. During the ironing the heat from the iron probably produces altered starch. With iodin, starch gives a blue-black color. This color reaction forms a test for either iodin or starch.

Enormous quantities of starch are used every year in making glucose and dextrin. It is also used in the laundry and as sizing material for finishing cloth. As a food it furnishes heat and energy. Nitric acid acts on starch to form *nitro-starch*, a compound having explosive properties. As an explosive this compound promises to become more common since starch can be prepared so cheaply.



Fig 133.—Sorting paper rags. (Courtesy of B. D. Rising Paper Co.)

**484.** Cellulose.— $(C_6H_{10}O_5)_x$ . Cellulose forms the basis of woody plants. Cotton and linen fibers are nearly pure cellulose. Wood is largely cellulose, and the cell-walls of various plants are made up of this important compound. Like starch, cellulose does not volatilize without decomposition, and it is insoluble in ordinary solvents. It dissolves in zinc chlorid solution and in an ammoniacal solution of copper oxid. We have already learned that nitric acid

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interacts with cellulose to form the basis of smokeless powder, collodion, and celluloid. Parchment paper is made by the action of sulfuric acid on cellulose. Further treatment with sulfuric acid converts cellulose into dextrin and glucose.

485. Paper.—Paper is made from cellulose which is obtained from various kinds of wood, from straw, and from

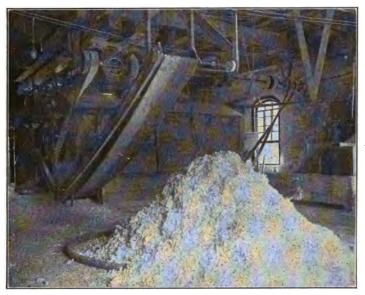


Fig. 134.—Rags cut and dusted ready for boiling. (Courtesy of B. D. Rising Paper Co.)

linen or cotton rags (see Fig. 133). In making paper from wood the raw material is first shredded and then treated with some reagent such as sodium hydroxid to dissolve the gummy substances and leave nearly pure cellulose. A better and stronger pulp is made by treatment with calcium bi-sulfite. If a white paper is desired some bleaching agent is used. When rags are used, they are cut into pieces and

dusted before boiling (Fig. 134). In the boiler of Fig. 135 about 12,000 pounds of rags are boiled at one time. To remove the color and impurities lime and soda are used during the boiling, which is continued several hours. In the treatment of either rags or wood pulp, the mass is next converted into pulp by being run through knives



Fig. 135.—A boiler in which 12,000 pounds of rags are boiled at one time. (Courtesy of B. D. Rising Paper Co.)

placed on rollers which match a set of knives on the bedplate (Fig. 136). From the beaters the pulp suspended in water is run onto screens (Fig. 137). From the screens it passes through rollers which dry it and press it into paper (Fig. 138). To increase the weight of paper such loading materials as clay, calcium sulfate, or barium sulfate are often added. If the weighting does not exceed 10 per cent., it is not considered an adulterant, although some papers contain 30 per cent. Paper that is to be used with ink is sized to close the pores and keep the ink from spreading. Rosin dissolved in sodium hydroxid and then precipitated with aluminum sulfate is often used for sizing. High-grade papers are sometimes sized with gelatine.



Fig. 136.—The beaters which convert the rags into pulp. (Courtesy of B. D. Rising Paper Co.)

486. Textiles.—Four fibers are extensively used in the textile industry. Silk and wool are animal fibers containing nitrogen as well as carbon, hydrogen, and oxygen. Wool also contains sulfur. Linen and cotton are nearly pure cellulose. The compound microscope furnishes the best method for identifying these fibers. The animal fibers, wool and silk, may be distinguished from the plant fibers,

linen and cotton, by chemical tests. Wool and silk dissolve in a hot solution of sodium hydroxid (5 per cent.), while cotton and linen are not much affected by such treatment. On the other hand, cold concentrated hydrochloric acid hardly affects wool and dissolves silk slowly, but it attacks the plant fibers more readily. While it is easy to distinguish cotton from linen by the use of the microscope, it is



Fig. 137.—Wet end of a Fourdrinier paper machine. (Courtesy of B. D. Rising Paper Co.)

not so easy by the use of chemical reagents, especially if the linen has been laundered a few times. Cold concentrated sulfuric acid dissolves cotton almost completely in 2 minutes, but attacks new linen only slightly in that time (Fig. 139).

487. Mercerized Cotton.—When cotton is immersed in a strong solution of sodium hydroxid it shrinks to about

three-fourths of its former length. If the cloth is stretched so that shrinkage can not occur when it is immersed in the sodium hydroxid solution, the nature of the fiber is changed. It becomes stronger and assumes a luster resembling silk. Cotton so treated is said to be *mercerized*, being named from John Mercer. Mercerized cotton takes dyes more readily than ordinary cotton.

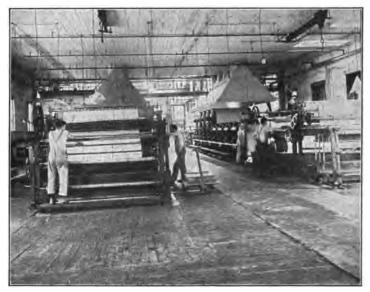


Fig. 138.—The cutter end of a Fourdrinier paper machine. (Courtesy of B. D. Rising Paper Co.)

488. Artificial Silks.—Several so-called artificial silks are now being manufactured. They are not silks at all, but they are made from cellulose so treated that it has a silky sheen. *Pyroxylin silks* are made by forcing a concentrated colloidal solution of nitrates of cellulose through very small capillary tubes under high pressure. The compounds solidify on contact with the air forming fine

silky threads. To render the fibers less inflammable they are de-nitrated by the action of some alkaline sulfid. Viscose silk is made in a similar manner, the solution of cellulose being prepared by treating wood fibers with sodium hydroxid and then adding carbon disulfid. Artificial silks are nearly as strong as natural silks and in some cases they have a more brilliant luster. Their tensile strength when they are wet is very much reduced. They are often known as luster-cellulose.

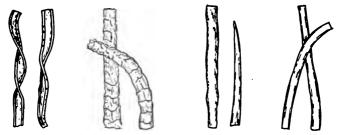


Fig. 139.—Fibers of cotton, wool, finen, and silk.

- 489. Cellulose Acetate.—This compound is formed by treating cellulose with anhydrous acetic acid. It is a viscous liquid. When it dries it forms a tough film that is waterproof and a non-conductor of electricity. It is less inflammable than the nitrates of cellulose, but more brittle. It finds use as an insulator, for making artificial horsehair, in airplane construction, auto goggles, gas masks, and in the manufacture of motion picture films.
- 490. Wool.—Wool is an animal fiber, usually obtained from the sheep, some species of goats, or from the llama, an animal found in the Andes mountains of South America. Mohair is made from the fleece of the Angora goat, and cashmere from the wool of a goat found in Thibet. Wool contains sulfur and nitrogen in addition to carbon, hydrogen, and oxygen. In scouring wool, suint and lanolin are obtained as by-products. Suint is a water soluble substance

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rich in potassium compounds. Lanolin is a wool-fat that is used in pharmacy as a vehicle for ointments.

Alkalis and oxidizing agents destroy woolen fabrics, hence a laundry soap containing much free base is not suitable for washing woolen, and chlorin is too strong an oxidizing agent to be used for bleaching woolen goods. Wool is quite hygroscopic, the amount of moisture absorbed upon the surface of the fiber being quite marked. Wool is sufficiently basic to combine readily with acid dyes without the use of a mordant. Wool fibers become brittle if heated much above 100°C.

491. Silk.—Silk also contains nitrogen, but unlike wool, it does not contain sulfur. Silk is obtained by unwinding the cocoons spun by the silk-worm. The silk-glue must be softened first in warm water before the fibers can be reeled. Like wool, silk is very hygroscopic. The determination of the amount of such water absorbed is technically known as conditioning. It may amount to as much as 30 per cent. of the weight of the silk. To make silk smooth and glossy the raw product, which is quite harsh, is treated with a warm soap solution to dissolve more of the silk-glue. the product is to be ecru silk, the washing is continued until the loss of weight is only 2 to 4 per cent. If all the glue is removed the loss in weight may be as much as 25 to 30 per cent. During the dveing of silks tin salts are often added. Such weighting of silk may more than double the weight of a fabric. A silk so heavily weighted or loaded may crack very quickly.

Silks are attacked by alkalis more readily than cotton; they dissolve in hydrochloric acid readily. Strong oxidizing agents destroy the fiber. Silk is bleached with sulfur dioxid, hydrogen peroxid, or a dilute solution of potassium permanganate.

492. Dextrin.—C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>. Dextrin is made by the action of saliva, diastase, or the pancreatic juice on starch. It

may be made commercially by heating starch, or by treating it with a dilute acid. Dextrin is a sticky substance used as a substitute for gum arabic in calico printing and as an adhesive for postage stamps and envelopes.

- 493. Pectin is a complex carbohydrate which forms with cellulose a compound known as pectocellulose. When certain fruits are boiled with water hydrolysis of this compound occurs, resulting in the formation of pectic acid. Pectic acid and its salts form a jelly when cooled. Fruits will not "jell" unless they contain pectin which may be partially transformed into pectic acid. Pectin is not present in over-ripe fruits, hence they can not form a jelly. Too long boiling decomposes the pectic acid of sour fruits and prevents the formation of jellies.
- 494. Gums.—These compounds are carbohydrates found in nature, usually secreted from the bark of certain trees. As a rule gums dissolve in water to form a mucilage, but are insoluble in alcohol. Gum arabic, or acacia, and gum tragacanth are two of the most common gums. They are used in preparing emulsions, in confectionery and lozenges, in calico printing, and in finishing cloth. Cherry gum is used for stiffening hats.
- 495. Resins.—The resins contain carbon, hydrogen, and oxygen. They are hard translucent solids, generally obtained as exudations from certain trees, or they may occur as fossil mineral substances. Unlike the gums, they are insoluble in water, but they dissolve in alcohol and turpentine. Rosin, copal, lac, amber, dammar, and sandarac are some of the most important resins. They find extensive use in the varnish industry. Asphalt is sometimes classed as a fossil resin.
- 496. Varnishes are made by dissolving resins in a suitable solvent. A good varnish should not be discolored by the action of water. It should form a hard, translucent, lustrous coating tough enough so it will neither crack easily,

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nor form a resinous dust when scratched with a sharp instrument. The properties depend upon the nature of the resin and upon the solvent used, some varnishes being tough and elastic, others being hard but somewhat brittle.

Spirit varnishes are made by dissolving a resin, usually lac, in alcohol. Such a varnish is known as shellac. It gives a hard surface and dries rapidly as the alcohol evaporates. Turpentine varnishes usually give a tougher coating; they are made by dissolving resins in hot turpentine. Oil varnishes are made by heating the melted resins with linseed oil or Chinese wood oil. They form excellent varnishes since the coat is very tough and resists the action of water very well. Copal is a resin largely used in making high-grade varnishes, while rosin is employed in the manufacture of cheap varnishes.

#### **FOODS**

- 497. Definition.—Any substance taken into the body proper that furnishes heat, energy, or nutrition may be termed a food. Before a food can be absorbed by the body and taken into the blood it must be in a fluid or semi-fluid condition. Digestion is the process of changing insoluble substances into soluble compounds or of producing emulsions, that may be readily absorbed. For example, starch is insoluble, but in the process of digestion it is changed by the action of a ferment into glucose, a soluble compound. Albuminoid substances are changed to peptone by the ferments pepsin and trypsin. Fats and oils are emulsified or saponified.
  - 498. Classification of Foods.—Foods are made up of the three classes of nutrients: Carbohydrates; proteins; fats and oils. The carbohydrates include starch and the sugars. The source of sugar we have already studied, and we also learned that corn and potatoes furnish large quantities of

starch. Other foods rich in starch are rice, flour, and all kinds of cereals.

Proteins, or albumins, are often called nitrogenous foods. They are very complex compounds containing carbon, hydrogen, oxygen, nitrogen, sulfur, phosphorus, and iron. When derived from different sources they vary slightly. Lean meat contains protein in the form of myosin. The white of egg is another form of protein known as albumen. When milk curdles, a white nitrogenous compound known as casein separates from the whey or liquid portion. The sticky substance in flour called gluten is another form of protein, while beans and peas contain protein in the form of legumin. Gelatin is a nitrogenous jelly obtained by long boiling of animal tissues. It can not wholly take the place of protein as a food.

Fats and oils are obtained from fat meat, butter, lard, and the oils from nuts and seeds.

To furnish mineral matter for the teeth and bones, such elements as calcium, phosphorus, and magnesium are needed. Iron is used in the blood, especially in the red blood cells, where it aids in carrying oxygen. It is obtained from such foods as spinach, lettuce, and other green vegetables. Mineral substances are also obtained from eggs, milk, cheese, and the outer covering of grains. Wholewheat bread has much more mineral matter than bread made from white flour. Food as prepared for use in most American families is apt to be deficient in mineral matter.

The outer covering of grains also contains more cellulose than the inner part and consequently more indigestible matter. This is believed to act mechanically as a laxative stimulant. It has been proven in Japan and the Philippines that the disease *beri-beri* is more common when rice from which the outer covering has been removed is used as a food. In the army and navy the brown rice

is now used instead of the white grain from which the hull has been polished.

Some foods contain all the nutrients in about the proportion they are needed in the body. Milk is such a food, having the following composition:

Water	Per cent.
Milk sugar	. 4–5
Fat	
Protein	. 3–4
Mineral ash	. 0.7

Meat and eggs both contain fat and proteins, but no carbohydrates. Bread consists largely of carbohydrates with some protein. With butter it forms quite a complete food.

499. Value of Foods.—Of several ways of determining food values, the measurement of the number of calories it can furnish is one of the most common. For example, it has been determined that one thick slice of bread will furnish 100 large calories of heat if completely oxidized. Sugar is a more concentrated food, 1½ teaspoonfuls furnishing 100 calories.

That the above method of judging food values is not satisfactory when used alone may be seen if we inquire the purpose of the various nutrients in food. The carbohydrates are usually completely oxidized, unless eaten in excess, and thus supply heat and energy to the body. Fats and oils are not so easily oxidized, but they yield more heat and energy than the carbohydrates. Proteins are eaten to replace worn-out tissues, and for building new tissues in a growing body. Thus it is easy to see that a carbohydrate diet might furnish all the heat and energy required daily, but growth and repair would be lacking. A mixed diet of fats and carbohydrates would still be

deficient in tissue-building properties. If the diet were wholly protein, a part of the food might be oxidized to supply the needed calories, and the remainder used for nutrition. This would be objectionable for two reasons: (1) Proteins are too expensive to be used for fuel; (2) the oxidation of fats and carbohydrates gives carbon dioxid and water only, while the oxidation of proteins leaves waste products that are excreted with difficulty. Thus an excess of protein results in overworked excretory organs, especially the kidneys. From the above statements the student can see that a proper diet should contain all the nutrients, proteins for nutrition, fats and carbohydrates for heat and energy.

Several other facts should also be considered in choosing a proper diet. For example, grass has much nutritious value, but the human stomach is not fitted to digest it. Wood has heat value but it is indigestible. In addition to a knowledge of heat values and composition of foods, the following questions should be asked: (1) What per cent. of the food is digestible? Some coarse vegetables contain a large per cent. of woody tissue that is entirely indigestible. On the other hand, a considerable amount of indigestible matter is desirable so the stomach and intestines may have bulky foods for peristalsis. (2) How much time and energy is required to digest a given food? The student must bear in mind that part of the food already digested must furnish the energy for digesting the following meal. If too much time and energy are required in digestion, the loss of energy may be equal to the gain. (3) Is the food liable to ferment? If food is not digested quickly fermentation may occur, producing gas and sour stomach. Starchy foods are especially liable to ferment.

In addition to all these factors, the complexity is increased by subjective conditions and the manner of life of the individual. To get the best results the student must study general principles and then modify them to fit his personal needs and his mode of living.

eaten raw, yet most foods are cooked before being eaten. Cooking serves at least three important purposes: (1) It makes the food more palatable. (2) Cooked foods are usually more easily digested than raw foods. (3) Cooking destroys disease-producing bacteria that may be present in the food. The cooking of protein foods coagulates the albumin and may in some cases make digestion rather more difficult. With starch, however, cooking breaks up the cells and makes digestion much easier; raw starch is apt to be indigestible, or digested with difficulty.

When meats are to be roasted they should be put in a. hot oven to coagulate the albumin on the outside and prevent loss of the juices. The heat may then be moderated as the steam in the interior continues the cooking. Broiled meats are seared over a naked flame for the same purpose. the juices being retained by the coagulated exterior. Baking generally requires a hot oven at the beginning for the same reason. In baking bread the interior of the loaf does not rise above the temperature of the steam. which really furnishes the heat for baking the inner part of the loaf. In boiling foods, if the water in which they are cooked is to be used for broth or soups, they may be put into cold water and heated slowly. If the water is not to be used, the foods should be put in hot water to prevent loss of nutritious matter. Fried foods are not easily digested as the particles become covered with grease, and fats are not digested until the food reaches the intestine. Rather unfortunately, many persons are fond of fried foods. the grease is hot when the food is introduced, coagulation occurs quickly and the grease does not soak into the food so readily.

501. Why Foods Spoil.—The decay of foods is brought

about by the action of three classes of plants; yeasts, molds, and bacteria (see Fig. 140). We have already learned that yeasts are capable of changing sugar into alcohol and carbon dioxid. Certain kinds of bacteria cause the decay of protein foods. In some cases disagreeable odors are given off by the gases formed, and usually the taste is very different. Ptomaines, poisonous bodies, are sometimes formed in animal foods by the action of bacteria. Although fats and oils are not so likely to spoil as the other nutrients, yet they sometimes become rancid by the action of bacteria. Molds



Fig. 140.—a, Yeasts; b, Mold; c, Bacteria.

and mildews are usually saprophytic plants, living and feeding on dead animal and plant tissues. Thus they gradually destroy the food. In the case of some molds poisonous substances are formed and the food is unfit to eat. In other cases certain molds are harmless, and in special varieties of cheese they may impart a desirable flavor.

With the exception of the molds these plants are very small, but they grow rapidly under favorable conditions. Moisture is necessary for the growth of all of them, while sunlight is unfavorable. In fact exposure to direct sunlight for 8 or 10 hours usually destroys them. Mold will not grow on dry bread, neither does sugar ferment unless it is in solution. The temperatures also affect the growth of these organisms. Most of them do not grow at 32°F. and few of them survive the temperature of boiling water. A temperature of 70° to 90°F. is very favorable to their rapid growth. Although these plants may live for a short

time without food, yet they can not multiply without it. They generally reproduce by simple division; thus one bacterium may divide to form two, these two may subdivide to form four, and so on. Under favorable conditions, temperature, moisture, and food supply, this fission may occur every 30 minutes. These organisms also develop spores which are so light that they are readily carried by the wind; in this manner they find their way into exposed foods, where they soon begin to grow. These spores often develop a thick wall and are capable of resisting drought and extremes of temperature.

502. Preservation of Foods.—Many ways of preserving food are in common use, all of them designed to destroy the organisms that promote decay or to prevent their coming into contact with the food.

One of the earliest methods of preserving food, and one that should be used more extensively in this country at the present time consists in dehydrating the food, or in removing the water that most foods contain so abundantly. should remember that the organisms that produce decay can not thrive unless moisture is present. Evaporated and condensed milk are more easily preserved than normal milk. on account of the removal of part of the water. In condensed milk sugar is also added as a preservative. Powdered milk is also coming into use, especially for cooking, baking, and the preparation of ready-mixed flours. It is made by partially evaporating the milk in vacuum pans and then spraying the remaining liquid through very small openings into a room heated by hot air. The rest of the water evaporates, leaving the milk as a white powder. foods preserved by drying are fruits, such as prunes, raisins, figs, apricots, etc. Corn and peas may be preserved in the same manner.

Canning food in tin cans or in glass jars is a common method of preserving foods. The food is heated to the

boiling point, or above in some cases, to kill the organisms that produce decay, and put into the container which is then sealed air-tight. Food properly canned will keep indefinitely. If the spores have not been killed by the heating the food will eventually be spoiled. The spores of yeast are more easily destroyed by heat than bacteria and their spores. The fermentation of fruits is usually caused by yeasts, since bacteria do not grow readily in an acidic solution. Vegetables are more difficult to preserve since the spores of the bacteria that cause them to spoil are not killed unless the boiling is continued at least 1 hour; or unless the food is boiled twice with an interval between sufficient to permit the spores to develop.

A concentrated sugar solution does not ferment, but a dilute solution is quickly acted upon by the wild yeasts that float in the air. Thus foods are *preserved* by adding to them large quantities of sugar.

Vinegar is another common substance in which the germs that produce decay do not grow readily. This liquid is used in preserving foods, the process being known as pickling.

Meats are preserved by the addition of salt, or by exposing them to the action of smoke for some time. The process is known as curing. The active preservative in the smoke is probably a cresol. When certain woods are used to produce the smoke, an agreeable flavor is imparted to the meat. Hickory bark is extensively used. Meats may be dried to preserve them.

Refrigeration is employed when foods are to be kept a comparatively short time. At the freezing temperature of water, or in a refrigerator near this temperature, bacteria multiply slowly and food may be kept for several days. Certain molds, however, may develop quite rapidly at this temperature. Enormous quantities of food are kept in cold storage. In such a plant cold brine circulates through

pipes in the storage rooms and keeps them at a temperature near the freezing point.

Many chemical preservatives are very efficient, but their use does not meet with popular favor. A small quantity of formaldehyd will keep milk sweet for days, but its use as a preservative is illegal. Salicylic acid and its sodium salt are excellent preservatives, but objection is made to their use. Sodium benzoate is a chemical preservative whose use in small quantities is permitted by the U. S. government. Sulfur dioxid and certain sulfites are used to bleach molasses, dried fruits, and to some extent as a preservative of certain foods. Potassium nitrate is used as a preservative in corned beef and smoked meats. Boric acid and borax occasionally find use as preservatives.

There is no doubt but that some of these preservatives have toxic properties. The chief objection to some of them lies in the fact that they destroy organisms that cause fermentation. Since pepsin in the stomach, and amylopsin, trypsin, and steapsin in the intestines are all ferments that produce digestion, it is claimed that chemical preservatives in food also interfere with digestion by arresting their action. On the other hand, ptomaines developed by bacteria in certain foods are deadly poisons and the products of decay are dangerous. Which is the lesser of the two evils, a possibility of disordered digestion from the action of the preservative, or illness from the poisonous products of decay, is a question that deserves more investigation than it has yet received, especially when we consider that the dose of sodium salicylate as given in the U.S. Pharmacopœia is 15 grains. The argument that canneries could put up partially spoiled foods if the use of chemical preservatives were generally permitted is further urged against them.

503. Food Adulterants.—Any substance mixed with a food to increase its weight or bulk is classed as an adulterant.

Preservatives are sometimes classed as adulterants. The substance used depends upon the nature of the food and is always some cheaper substance. Since the adulterant is added with intent to deceive, it generally very closely resembles the pure product. While oleomargarine may be used to adulterate butter, yet it is needless to test oleomargarine to see whether it has been adulterated with butter. Meats and eggs are seldom adulterated, although inferior cuts of meat may be substituted for more expensive ones. is sometimes adulterated with gypsum and low-grade flours are substituted for high-grade wheat flour. Olive oil is frequently adulterated with cotton-seed oil. Water is the most common adulterant of milk. Extracts are frequently adulterated with cheaper substitutes. The adulteration of foods in the United States is not nearly so common as it was before the Pure Food Law of 1906 was enacted.

- 504. Coal-tar Compounds.—Several coal-tar compounds are used in foods and many important drugs are obtained from this source. Seven of the coal-tar colors are considered harmless and the United States permits their use for coloring candies, jellies, butter, and other foods. Saccharin is a coal-tar product more than 500 times as sweet as cane-sugar. It was at one time used quite extensively to sweeten canned goods, but at the present time such use is illegal. Coumarin and artificial vanillin are coal-tar products used as flavors. We have already learned that benzoic acid and salicylic acid are preservatives. Salicylic acid and its salts are also used as medicine. Aspirin and acetanilid are used in head-ache powders and anti-pain pills, but the use of the latter especially is attended with considerable danger.
- 505. Disinfectants and Antiseptics.—A chemical substance that destroys disease-producing bacteria is known as a disinfectant. Formaldehyd is one of the best disinfectants, since its vapor so readily penetrates to all parts of a room. Other substances often used are sulfur dioxid,

chlorid of lime, carbolic acid, cresols, and bi-chlorid of mercury.

An antiseptic is a substance used to prevent or check the growth of putrefactive, or pus-forming bacteria. It differs from a disinfectant in the fact that it may be applied to living tissues without much injury to them. Iodin, iodoform, hydrogen peroxid, boric acid, and very dilute solutions of carbolic acid and bi-chlorid of mercury are commonly used antiseptics. Of course these substances are also preservatives. Together with other chemicals they are sometimes classed as germicides.

506. Alkaloids.—The alkaloids are nitrogenous compounds obtained from plants. Since they often give to a plant its chief characteristics they are sometimes known as the active principles of plants. Many of them are used as medicines, although with few exceptions they are very poisonous. They are analogous to ammonia from the fact that they unite with acids by direct addition. Quinine is an alkaloid extracted from Cinchona trees. Its hydrobromid and sulfate are extensively used in medicine, especially in the treatment of malaria. Cocaine, obtained from coca leaves, is an important local anesthetic. is an active stimulant found in coffee and tea. Codeine is an alkaloid extracted from opium, as is morphine. Both alkaloids are used to allay pain. Paregoric and laudanum are prepared from opium. Nicotine is a very poisonous compound found in tobacco. Strychnine is an active poison that occurs in nux vomica. Atropine is an alkaloid found in belladonna. It is used by optometrists to dilate the pupil of the eye. Ptomaines are alkaloids formed in dead animal tissues.

While such alkaloids as morphine and cocaine are very valuable drugs, they should never be used unless prescribed by a physician as they are habit-forming drugs that produce very disastrous results.

507. Poisons and Antidotes.—In addition to the alkaloids mentioned in the preceding paragraph, many metallic compounds are poisonous. In fact soluble compounds of arsenic, antimony, barium, zinc, tin, lead, copper, mercury and silver are all more or less active poisons. Several phosphorus compounds are poisonous, and certain groups of elements like the cyanid group are extremely poisonous.

An antidote is some substance used to counteract a poison. It may destroy the effect of the poison by neutralization, or it may unite with it to form an insoluble compound which is not absorbed by the digestive tract. Three general rules may be given that should be followed in case of poisoning: (1) Give an emetic to produce vomiting. Ipecac is usually most successful, as it contains the alkaloid emetine. a very nauseating compound. (2) Give an antidote, if the nature of the poison is known. (3) Give a purgative, such as castor oil or Epsom salts, to remove the poison from the intestines. Very often the poison is unknown and no special antidote can be given. Fortunately albumin forms an insoluble compound with the salts of most metals, and the whites of eggs and milk may be used freely, as the treatment can do no harm. If a narcotic poison, such as opium, morphine, or nicotine, has been taken, a stimulant like strong coffee should be given in quantity. Alcohol is not a stimulant, but a narcotic. In any case, do not let the person sleep, but keep him moving. The inhalation of ammonia is beneficial. For a stimulant poison like strychnine, a sedative such as sodium bromid may be used, or a narcotic like chloral.

For acid poisoning, use sodium bi-carbonate, soap-suds, chalk, or magnesia.

For alkali poisoning, use vinegar, lemon juice, or orange juice.

Arsenic.-Milk; raw eggs; freshly precipitated ferric hy-

droxid. Such rat poisons as "rough on rats" contain arsenic, as does also Paris green.

Bichlorid of Mercury.—For this and other mercury compounds use milk freely; white of eggs; zinc sulfate.

Carbolic Acid.—Alcohol; raw eggs; Epsom salts.

Hydrocyanic Acid.—Ferrous sulfate followed by small quantities of potassium carbonate; artificial respiration; inhaling ammonia.

Iodin.—Starchy foods in abundance; "hypo."

Lead Salts.—Epsom salts; milk; albumin.

Phosphorus.—Copper sulfate; Epsom salts. Avoid oils. Potassium Cyanid.—Ferrous sulfate. Artificial respiration.

Silver Nitrate.—Sodium chlorid, or common table salt.

Tartar Emetic.—Milk; eggs.

### SUMMARY

The carbohydrates contain carbon, hydrogen, and oxygen; they include sugars, starch, cellulose, dextrin, and certains gums.

Cane-sugar, beet-sugar, and maple-sugar all contain sucrose,  $C_{12}H_{22}O_{11}$ . When sucrose is heated to 210°C. it is converted into caramel. When treated with acids inversion occurs, resulting in the formation of dextrose and levulose. These sugars are isomeric; they have the same formula, the same molecular weight, but differ in properties.

Lactose, or milk sugar contains water of crystallization. All the sugars are used as foods.

Starch is a white amorphous substance made by plants that have green coloring matter. It is a good food, it finds use in the laundry, and in finishing cloth. With iodin it produces a blue-black color.

Cellulose forms the framework for woody plants. It is

used in the textile industry, for making explosives, paper, celluloid, and artificial silk.

Dextrin is made from starch. It finds use as a mucilage and in calico printing.

Gums and resins also contain carbon, hydrogen, and oxygen. The gums are water soluble or at least partially so, but insoluble in alcohol. The reverse is true of the resins. Resins are used in the varnish industry. Spirit varnishes consist of shellac dissolved in alcohol. Turpentine varnishes consist of turpentine in which a resin has been dissolved. Oil varnishes are made from linseed oil or China wood oil and such resins as copal, amber, dammar, and sandarac. Rosin is used in cheap varnishes.

A substance taken into the body that supplies to it heat, energy, or nourishment is termed a food. Digestion is the process of changing insoluble foods into soluble compounds.

Carbohydrates, proteins, and fats or oils form the three classes of nutrients needed by the body. Mineral matter is also essential to the body.

The value of a food may be determined by the number of calories it yields upon oxidation, by the relative proportion of the three nutrients it contains, by the ease with which it is digested, by the amount of indigestible matter, and by its liability to ferment.

Foods are cooked to make them more palatable, to promote digestion, and to destroy any bacteria that may be present. Baking, roasting, and boiling are all excellent methods of cooking foods.

Bacteria, yeasts, and molds are three types of microörganisms that cause food to ferment or decay. They thrive at moderate temperature, on a moist surface, protected from sunlight, provided they have plenty of food material.

Foods are preserved by destroying these organisms and preventing their coming into contact with the food thus

sterilized. The various methods include drying, canning, preserving with sugar, pickling, salting and smoking, cold storage, and the use of chemical preservatives.

A substance mixed with a food to increase its weight or its bulk is termed an adulterant. Chemical preservatives are often classed as adulterants. The adulterant used is always some cheaper product.

Both disinfectants and antiseptics destroy bacteria that produce disease. Antiseptics are of such a nature they may be applied to living tissues.

An alkaloid is a nitrogenous compound obtained from plants. They find use in medicine.

An antidote is a substance used to counteract a poison. In case of poisoning give an emetic, then an antidote if possible, and follow with a cathartic to remove the poison from the intestines.

## QUESTIONS AND PROBLEMS

- 1. What is a carbohydrate? Name at least three, giving their formulas.
- 2. What is meant by the inversion of sugar? How is it produced?
- 3. Why is vinegar added to a candy that is to be pulled? Would it do as well to start with glucose?
  - 4. Discuss the commercial importance of cellulose.
  - 5. How does "smokeless powder" differ from pyroxylin silk?
  - 6. What is meant by loading paper? By sizing paper?
- 7. How would you distinguish cotton from linen? Cotton from wool? Wool from silk? Silk from luster-cellulose?
- 8. What are the characteristics of a good varnish? How would you test a varnish?
- 9. Why should a proper menu contain all the various food nutrients?
- 10. What purpose does each of the three nutrients serve in the body?

- 11. Why do we relish buckwheat cakes with butter and syrup more in January than in July?
  - 12. What is the objection to eating raw potatoes? Raw meats?
- 13. Outline several methods of preserving foods. Upon what principle is each method based?
  - 14. Why are chemical food preservatives also good antiseptics?
  - 15. Give examples of several food adulterants.
- 16. What principles are involved in the use of antidotes to poisons?

Topics for Reference.—Manufacture of textiles. Food preservatives (Government bulletins). Bomb Calorimeter. Atwater-Rosa Calorimeter.

### APPENDIX A

# GLOSSARY OF CHEMICAL TERMS, MINERALS, AND ORES

**Absorption.**—The process of taking up a substance by chemical action or some form of molecular attraction.

Acid.—A compound whose water solution contains positive hydrogen ions.

Acidify.—To make a substance acid.

Acidulate.—To add acid to a solution or substance until it is no longer alkaline.

Actinic.—That portion of the sun's spectrum which produces chemical effects.

Adsorption.—The adhesion of gases or substances in solution to the surfaces of solids.

Aeration.—The exposure of a substance to the chemical action of the air.

Alabaster.—A fine-grained variety of gypsum.

Algae.—The popular name for all classes of sea-weeds.

Alkali.—Any substance having marked basic properties.

Allotropic.—Capable of existing in two or more different forms.

Alloy.—A solid solution of two or more metals.

Alundum.—An artificial oxid of aluminum used as an abrasive,

Amalgam.—An alloy, one constituent of which is mercury.

Amorphous.—Without crystalline form. Non-crystalline.

Amphoteric.—Capable of acting as either an acid or a base.

Analysis.—The separation of a compound into its elements.

Anhydrous.—Without water. A substance from which water has been removed is anhydrous.

Anode.—The positive electrode of an electrolytic cell.

Antidote.—A substance used to counteract the effect produced by a poison.

Antiseptic.—A substance used to prevent decay.

Apatite.—A mineral consisting of calcium phosphate.

Aragonite.—A mineral that crystallizes from a solution of calcium carbonate, forming prismatic crystals.

Argentite.—An important ore of silver consisting of the sulfid.

Asbestos.—A fibrous mineral; a silicate of calcium and magnesium.

Association.—The aggregation of like molecules to form more complex molecules.

Atom.—The smallest particle of matter that can enter into combination.

Azurite.—A beautiful native carbonate of copper.

Barite.—A native sulfate of barium.

**Barometer.**—An instrument used to measure the pressure of the atmosphere.

Bauxite.—A hydrated oxid of aluminum. The chief ore of aluminum.

Beri-beri.—An acute disease caused by a diet deficient in mineral matter

Binary.—A compound consisting of two elements.

Bornite.—A copper ore containing sulfids of iron and copper.

By-product.—A secondary product obtained in manufacturing, in addition to the chief product.

Calamite.—A natural silicate of zinc.

Calcine.—To heat strongly.

Calcite.—A crystallized form of calcium carbonate found in nature.

Calorie.—The unit of heat required to raise the temperature of 1 gram of water 1°C.

Carborundum.—A carbid of silicon used as an abrasive.

Carnallite.—A hydrated chlorid of potassium and magnesium. The chief ore of magnesium.

Cassiterite.—A native oxid of tin which forms the chief ore of that metal.

Catalysis.—The acceleration of a chemical reaction by the presence of some substance that does not appear to enter into the reaction.

Cathode.—The negative electrode of an electrolytic cell.

Celestite.—A native sulfate of strontium.

Cerite.—A silicate of cerium.

Chalcocite.—A native sulfid of copper.

Chalcopyrite.—A sulfid of copper and iron that forms a valuable copper ore.

Chromite.—An important ore of chromium.

Cinnabar.—Mercuric sulfid, the most important ore of mercury.

Coagulum.—A bulky precipitate used to clarify liquids.

Colloid.—A non-crystalline substance of a gelatinous nature.

Coquina.—An aggregate formed from shells of marine animals.

Corrosion.—The action of chemicals that results in the formation of rust.

Corundum.-An oxid of aluminum.

Cryolite.—A native fluorid of sodium and aluminum.

Cupel.—A small cup, made of bone ash, used to separate lead from silver.

Decrepitate.—To crackle, as certain salts do when heated.

Deflagrate.—To burn rapidly or suddenly.

Deflocculated.—Very finely divided.

Dehydrated.—Deprived of its water, or of the elements that comprise water.

Deliquescence.—The absorption of water from the air.

Density.—The weight per unit volume.

Desiccate.—To dry.

Detergent.—A substance that has cleansing properties.

**Detonation.**—An explosion caused by the nearly instantaneous decomposition of the explosive.

Dialysis.—The separation of colloids from crystalloids by means of a membrane.

Diffusion.—The intermingling of fluids without regard to the laws of weight.

Disinfectant.—A substance used to destroy the bacteria that produce decay or disease.

Disintegration.—The decomposition of a substance into simpler substances.

Dissociate.—To break up a compound into its constituents.

Dolomite.—A native carbonate of calcium and magnesium.

Ductility.—That property of a substance by virtue of which it may be drawn into wire.

Ebullition.—Rapid boiling.

Effervescence.—The rapid evolution of a gas, as when an acid is poured on a carbonate.

Efflorescence.—The formation of a powdery crust on the surface of a crystal when it loses its water of crystallization.

Electrode.—Either terminal of a battery.

**Electrolysis.**—The decomposition of a compound by means of an electric current.

Electron.—A negatively charged particle of matter.

Feldspar.—A silicate of potassium and aluminum that forms clay upon weathering.

Filler.—A cheap substance used to increase the bulk of a compound.

Fixed.—Non-volatile.

Flocculent.—Flaky.

Fluorescence.—The property some substances have of emitting light when exposed to ultra-violet light, radium, or the X-rays.

Fluorite.—A fluorid of calcium.

Flux.—A substance used to lower the melting point of another with which it is mixed.

Fungicide.—A substance used to destroy fungi.

Galenite.—The native sulfid of lead that forms its chief ore.

Galvanized.—Coated with a layer of zinc.

Gangue.—The earthy impurity found with metallic ores.

Genthite.—A native silicate of nickel.

Germicide.—A substance used to destroy bacteria.

Gravimetric.—An analysis in which the amount of the constituents is determined by weighing.

Gypsum.—A sulfate of calcium.

Halite.—The name of the mineral sodium chlorid.

Halogen.—Salt producer.

Hematite.—A very important ore of iron having the formula Fe<sub>2</sub>O<sub>2</sub>.

Hydrate.—A compound formed by the union of water with some substance.

Hydrocarbon.—A compound containing only hydrogen and carbon.

Hydrogenation.—The treatment of a substance with nascent hydrogen.

Hydrolysis.—The decomposition of a compound by the action of water.

Hydroxyl.—A name given to the OH radical.

Hygroscopic.—Readily absorbing moisture.

Ignite.—To set on fire or to heat strongly

Impervious.—Impenetrable; not porous. Impregnated.—Thoroughly saturated with

Incandescent.—Heated until it glows.

Infusoria.—An order of minute animal organisms.

Inhalation.—Act of inspiration, or drawing breath into the lungs.

Insecticide.—Any substance used to destroy insects.

Insulator.—A substance that does not readily conduct heat or the electric current.

Ion.—An atom or a group of atoms that serves as a carrier of electricity.

Ionization.—The dissociation of a compound into its ions.

Isinglass.—A soluble glue made from the air-bladder of certain fishes.

Isomeric.—Two compounds having the same percentage composition and the same molecular weight, but differing in properties, are isomeric.

Isomorphous.—A similarity of crystalline form between similar compounds.

Kainite.—A natural salt rich in potassium sulfate.

Kaolin.—A fine white clay used in the porcelain industry.

Kelp.—Sea-weeds that contain iodin and potassium as mineral matter.

Kinetic.—Moving, or pertaining to motion.

Leach.—To treat with water in order to dissolve the soluble portions of a substance.

Limonite.—An important ore of iron.

Lixiviate.—Used in the same sense as leach.

Magnesite.—A natural carbonate of magnesium.

Magnetite.—A valuable ore of iron, having the formula Fe<sub>3</sub>O<sub>4</sub>.

Malachite.—A beautiful green carbonate of copper.

Malleability.—That property of matter by virtue of which it may be hammered or rolled into sheets.

Manganite.—A hydrated oxid of manganese found in nature.

Meerschaum.—A hydrated silicate of magnesium used in making pipes.

Mica.—Any one of a group of silicate minerals that cleaves readily into thin elastic sheets. Incorrectly called isinglass.

Millerite.—A natural sulfid of nickel.

Miscible.—Capable of being mixed. Mutually soluble liquids are said to be miscible.

Monazite.—A mineral containing thorium and cerium.

Monoclinic.—A system of crystallization in which one axis is inclined so that it does not meet the other axes at right angles.

Nascent.—An element is in the nascent state when it is just liberated from a compound.

Native.—Occurring free in nature.

Nitrogenous.—Containing nitrogen.

Noxious.—Injurious or harmful.

Occlusion.—The absorption of gases by metals.

Opal.—A precious stone consisting of silica.

Orpiment.—A sulfid of arsenic found in nature.

Osmosis.—The diffusion of fluids through membranes.

Oxid.—A binary compound consisting of oxygen and some other element.

Oxidation.—The union of oxygen with some other substance. An increase in the valence of the metallic element of a compound.

Pathogenic.—Disease producing.

Peristalsis.—A peculiar successive contraction of muscular fibers.

Phosphorescence.—A faint light emitted by certain substances during a very slow oxidation.

Pneumatic.—Pertaining to gases.

Precipitate.—A substance separated from a solution as a result of some physical or chemical action.

Ptomaine.—A poisonous alkaloid formed by putrefactive bacteria.

Pyrites.—A yellow crystalline mineral having the formula FeS<sub>2</sub>.

Pyrolusite.—An important ore of manganese.

Pyrotechnics.—The making and use of fire works.

Radical.—A group of elements that behaves chemically as a single element.

Rancid.—Having a disagreeable odor and taste.

Reagent.—A substance used in chemistry to bring about a chemical change.

Reduction.—The abstraction of oxygen from a compound.

Refractory.—Infusible, or fusible with great difficulty.

Reverberatory.—A furnace in which the flame is diverted from the roof on the material to be heated.

Roast.—To heat strongly in the air, thus converting sulfids and carbonates of minerals into oxids.

Saleratus.—A name given to potassium bi-carbonate, and now generally referring to sodium bi-carbonate.

Saprophytic.—A class of plants that feed upon dead organic matter. Sedative.—A remedy used to allay pain.

Self-protective.—A term used in chemistry of metals that form an adherent tarnish which protects them from further corrosion.

Siderite.—A carbonate of iron found in nature.

Slag.—The impurities of an ore removed during the process of smelting.

Slake.—To mix with water in such a way that a chemical reaction occurs.

Smithsonite.—A natural carbonate of zinc.

Specific.—As used in physics or chemistry the word implies or designates a ratio.

Spectra.—Images formed by the dispersal of a beam of light in passing through a prism.

Spectroscope.—An instrument used for examining spectra.

Sphalerite.—The most abundant ore of zinc; it has the formula ZnS.

Spontaneous.—Proceeding without external force or stimulus.

Stable.—Not readily decomposed.

Stalactite.—A deposit of mineral matter, chiefly calcium carbonate, hanging from the roof or walls of caverns.

Stalagnite.—A deposit of mineral matter formed on the floor of caverns.

Stibnite.—A natural sulfid of antimony.

Strontianite.—A carbonate of strontium that forms one of its important ores.

Sublimate.—A product formed by the process of sublimation.

Superheated.—A vapor heated above the temperature necessary to keep it from condensation.

Supernatant.—The liquid that stands above a precipitate.

Sylvite.—A chlorid of potassium. One of the important potassium ores.

Talc.—A silicate of magnesium used in preparing talcum powder.

Tarnish.—Any form of corrosion that occurs at the surface of metals.

Tenacity.—Tensile strength. The property some substances have that makes it difficult to pull them asunder.

Topaz.—A natural silicate of aluminum used as a gem.

Toxic.—Poisonous.

Tuyères.—A nozzle through which air is delivered to a blast furnace.

Vehicle.—The liquid or medium in which a paint or varnish is suspended.

Viscid.—Glutinous or sticky.

Vitrified.—Converted into a glassy substance by heat or partial fusion.

Volatile.—Capable of being easily vaporized.

Volumetric.—An analysis in which the amount of the constituents is determined by measuring their volume.

Witherite.—A barium mineral having the formula BaCO<sub>3</sub>.

Wolframite.—A tungstate of iron and manganese used as a source of tungsten.

Zincite.—An ore of zinc having the formula ZnO.

# APPENDIX B

### BIOGRAPHICAL SKETCHES

The following biographical sketches are so arranged as to give the student a brief outline of the historical development of chemistry. The first group contains some of the leading alchemists. In the second group are found the chemists of the phlogistic period. Modern chemistry dates from the time of Lavoisier. In all cases the arrangement is chronological.

#### THE ALCHEMISTS

Geber.—Arabian alchemist of the 8th century. Considered the founder of alchemy. Discovered aqua regia. Author of many works of alchemy.

Bacon, Roger (1214-1294).—An English philosopher who was so far in advance of his time that he was persecuted for dealing in the black art of magic.

Valentine, Basil.—A German alchemist of the 15th century. His writings are a mixture of scientific observation and mysticism.

Paracelsus (1493–1541).—A German physician and alchemist. Called the Father of Medicine. Introduced alcoholic preparations, lead and antimony compounds, and the "vitriols" as remedies.

Van Helmont (1577–1644).—A Belgian physician and alchemist. Studied gases and distinguished several kinds. Used melting ice and boiling water as temperature standards.

Mariotte, Edme (1620–1684).—A French physicist whose name in France is associated with the law showing the relation between gas volumes and pressures. (More often known as Boyle's law.)

Boyle, Robert (1627-1691),—An Irish chemist who formulated Boyle's law. Defined "element," "mixture," "compound," and "analysis." Discovered wood alcohol and phosphoric acid.

Becher, Johann J. (1635-1682).—Advocated the theory that a substance in burning unites with "terra pinguis." This theory gave rise to the phlogiston theory.

#### THE PHLOGISTIC PERIOD

Mayow, John (1645-1679).—An English chemist who preceded Priestley and Lavoisier in speculating on the nature of combustion. Knew that something from the air unites with metals when calcined.

Stahl, Georg Ernest (1660-1734).—Physician to King of Prussia. Founder of the phlogiston theory of combustion.

Marggraf, A. S. (1709-1782).—Pupil of Stahl. Noted that phosphorus increases in weight when burned. Introduced use of microscope in analysis. Discovered beet sugar.

Black, Joseph (1728-1799).—A Scotch chemist. Prepared carbon dioxid by heating carbonates. Supported Lavoisier's theory of combustion.

Cavendish, Henry (1731-1810).—An English chemist. Discovered hydrogen. Studied volumetric composition of water, air, etc.

Priestley, Joseph.—See portrait. Opposite page 22.

Bergmann, T. (1735–1784).—Swedish professor. Developed blowpipe mineral analysis. Discovered molybdenum and tungsten.

Scheele, Carl Wilhelm (1742–1786).—A Swedish chemist. His brilliant discoveries include tartaric acid, oxygen, chlorin, barium, glycerin, manganese, fluorin, aldehyd; also citric, malic, prussic, lactic, uric, pyrogallic, and oxalic acids. In working with arsenic he discovered the arsenite of copper, Scheele's green.

LeBlanc, Nicolas (1742–1806).—A French chemist who discovered a method of making sodium carbonate from sodium chlorid. His plants were destroyed during the French revolution.

#### MODERN CHEMISTS

Lavoisier, Antoine Laurent.—See portrait. Opposite page 22.

Charles, Jacques A. C. (1746–1823).—A French physicist. First to employ hydrogen for inflating balloons. In 1787 formulated Charles' law.

Berthollet, Claude Louis (1748–1822).—A French chemist. Studied ammonia, hydrogen sulfid, and other gases. Showed bleaching action of chlorin. Showed effect of chemical equilibrium and advocated the laws that enable the chemist to forecast chemical actions that deal with metathesis.

Proust, Joseph Louis (1754–1826).—A French chemist. Put law of definite proportions on a firm basis by quantitative experiments. Discovered glucose.

Dalton, John.—See portrait. Opposite page 110.

Henry, William (1774-1836).—An English chemist. Henry's law

stating that the amount of gas absorbed by a liquid varies as the pressure.

Avogadro, Amadeo (1776-1856).—An Italian physicist. Theory relating to the relative number of molecules in equal volumes of gases.

Thenard, L. J. (1777-1857).—French professor. Worked with Gay-Lussac in making bleaching powder, white lead, and chlorin. Discovered hydrogen peroxid and hydrogen fluorid.

Davy, Sir Humphrey.—See portrait. Opposite page 140.

Gay-Lussac, Joseph Louis.—See portrait. Opposite page 110.

Berzelius, Jons Jakob.—See portrait. Opposite page 140.

Dulong and Petit.—Joint discoverers of the law that the specific heat times the atomic weight of an element is a constant quantity.

Faraday, Michael.—See portrait. Opposite page 366.

Dumas, Jean Baptiste (1800–1884).—A French chemist known best by his researches on atomic weights. Vapor density determinations.

Wohler, Friedrich (1800–1882).—A German chemist. One of the founders of organic chemistry. Prepared the first synthetic organic compound in 1828. Isolated aluminum, beryllium, yttrium, and titanium. Discovered hydroquinone and calcium carbid.

Boussingault, Jean Baptiste (1802-1887).—A French chemist interested in agricultural chemistry.

Liebig, Justus Von (1803–1873).—A German chemist. Devised present system of organic analysis. Analyzed alkaloids. Discovered chloral, chloroform, and aldehyd. Founder of agricultural chemistry.

Graham, Thomas (1805–1869).—An English chemist. Researches included the diffusion of gases and substances in solution. Discovered dialysis as a method of separating crystalloids and colloids. Rate of osmosis.

Bunsen, Robert Wilhelm.—See portrait. Opposite page 236.

Bessemer, Sir Henry (1813–1898).—English inventor. Developed the Bessemer process for making steel. Invented process for compressing graphite in the making of lead pencils; a process for molding type; and a process for embossing velvet.

Stas, J. S. (1813-1891).—Professor at Brussels. Very accurate determinations of atomic weights. Spectra of alkaline earths.

Pasteur, Louis (1822-1895).—A French chemist. Founder of stereo-chemistry. Showed that micro-organisms cause fermentation, and that germs in the air cause putrefaction. Studied production of serums.

Siemens, Sir Wm. (1823-1883).—An English metallurgist. Devised water meter and the regenerative furnace.

Kekule, Friedrich August (1829–1896).—A German chemist who specialized in organic chemistry. Showed the tetravalency of carbon. Devised the structural formula for benzol.

Raoult, Francois Marie (1830–1901).—A French chemist. Showed that the molecular weight of a compound may be found by freezing-point and boiling-point methods.

Cailletet, Louis Paul.—A French chemist. Succeeded in 1877 in liquefying both oxygen and nitrogen.

Crookes, Sir William (1832-—).—An English physicist and chemist. His method of producing high vacua made incandescent lighting possible. Discovered thallium. Crooke's tubes. New method of studying spectroscopy.

Nobel, Alfred Bernard (1833-1896).—A Swedish inventor. Invented dynamite and smokeless powder. Founder of Nobel prize fund.

Mendelejeff Dimitri Ivanovitch.—See portrait. Opposite page 236.

Morley, Edw. Williams (1838——).—An American chemist. Research work on the weigh of gases. Determination of ratio of combining weights of hydrogen and oxygen.

Perkin, Sir William Henry (1838–1907).—An English chemist. Discovered mauve dye in 1856 and thus founded the synthetic coaltar dye industry. Synthesis of tartaric acid and coumarin.

Solvay, Ernest (1839-—).—A Belgian chemist. Devised a process for making sodium carbonate and sodium bi-carbonate.

Dewar, James (1842- —).—English chemist. Studied physiological action of light and liquefaction of gases. Invented the Dewar bulb as a container. With Sir Frederick Abel invented cordite.

Pictet, Raoul (1842- —).—A Swiss chemist. Studied liquefaction of gases and low temperatures.

Rayleigh, Lord (John Wm. Strutt) (1842- —).—An English physicist. In 1894 with Ramsay he discovered argon. Nobel prize in physics in 1904.

Babcock, Stephen Moulton (1843–1916).—An American chemist. Studied milk and milk products. Invented Babcock tester. Professor of chemistry at Univ. of Wisconsin. Chemist for Wis. Agricultural Exp. Station.

Atwater, Wilbur Olin (1844-1907).—An American chemist. From '94 to '05 had charge of the nutrition investigations of U. S. Dept. of Agriculture. With Rosa, inventor of respiration calorimeter.

Becquerel, Antoine Henri (1852-1908).—A French physicist.

Noted for his studies in invisible radiations. Nobel prise in physics in 1903 was awarded to Becquerel, M. and Mme. Curie.

Fischer, Emil (1852-—).—German chemist. Researches in synthesis of sugars and organic compounds. Nobel prize in 1902.

Frasch, Herman (1852-1914).—An American chemist. Desulfurization of petroleum. Method for extracting Louisiana sulfur.

Moissan, Henri (1852-1907).—French chemist. Isolated fluorin. Produced artificial diamonds. Electric furnace. Simplified production of acetylene.

Ramsay, William (1852-1916).—English chemist. Discovered helium, neon, krypton, and xenon. Discovered niton, or radium emanation. With Soddy, showed that helium is a decomposition product of radium. Nobel prize in 1904.

Van't Hoff, Jacobus Henricus (1852–1911).—A Dutch physical chemist. Applied Avogadro's theory to dilute solutions.

Ostwald, Wilhelm (1853-—).—A German chemist who investigated physical chemistry. Nobel prize in 1909.

Acheson, Edward Goodrich (1856- —).—Inventor of carborundum, siloxicon, and a process of making graphite. Perkin medal in 1910.

Thomson, Joseph John (1856——).—English physicist. Development of electron theory of electricity. Theories of radio-activity.

Castner, Hamilton Young (1857–1899).—American chemist. Reduced price of aluminum by a new method of extraction. Devised an electrolytic method for preparing sodium hydroxid from sodium chlorid.

Arrhenius, Svante.—See portrait. Opposite page 184.

Hall, Charles Martin.—See portrait. Opposite page 184.

Nernst, Walther (1864——).—A German physical chemist. Invented Nernst incandescent lamp. Invented quadrant electrometer.

Curie, Marie Sklodowska.—See portrait. Opposite page 366.

Duncan, Robert Kennedy (1868–1914).—New process for making phosphorus, for making low melting glass, and for decorating glass. Established industrial fellowships in Universities of Kansas and Pittsburgh. Author of Chemistry of Commerce, The New Knowledge, and Chemical Problems of To-day.

Richards, Theodore William (1868——).—An American chemist. Best known for his work in revising atomic weights, Studied compressibility of atoms and atomic volumes. Nobel prize in 1914.

Rutherford, Ernest (1871-—).—Former Professor of physics at McGill University. Now at University of Manchester. Studied radio-activity and ionization of gases. Nobel prize in 1908.

### APPENDIX C

### BIBLIOGRAPHY

Several reference topics are suggested at the end of the various chapters. Beneficial results may be secured by assigning these topics to students somewhat in advance and later asking for oral or written reports. The author would suggest that students be taught the use of the "Readers' Guide." The following magazines will be found especially helpful: The Scientific American; School Science and Mathematics; the Popular Science Monthly; the World's Work; the Independent; and the Illustrated World.

Any good encyclopedia furnishes ready reference and usually contains some material that can be used to supplement the text. The catalogs of manufacturing firms furnish a very fertile field for detailed information on various topics. The bulletins of the Dept. of Agriculture contain expert information that is often exceedingly useful to the student. Some of the bulletins are free; for others a slight charge is made, usually five or ten cents. By sending to the Dept. of Agriculture at Washington, a list of available bulletins may be obtained.

The following bibliography includes a list of books that will be useful for more extensive reading or study:

ALLYN.—Elementary Applied Chemistry. Ginn & Co.

Bailey.—Text-book of Sanitary and Applied Chemistry. The Mac Millan Co.

BOTTLER.—Modern Bleaching Agents. D. Van Nostrand Co. BROWNLEE.—Chemistry of Common Things. Allyn & Bacon. BRUCE.—Foods and Their Adulterants. D. Van Nostrand Co.

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The MacMillan Co.

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# APPENDIX D

### USEFUL TABLES

### TABLE 1.-METRIC-ENGLISH EQUIVALENTS

- 1 inch equals 2.54 centimeters.
- 1 ounce equals 28.35 grams.
- 1 pound equals 453.6 grams.
- 1 meter equals 39.37 inches.
- 1 liter equals 1.056 liquid quarts.
- 1 kilogram equals 2.2046 pounds.

TABLE 2.—THERMOMETER CONVERSION TABLE

To convert Centigrade readings into the corresponding Fahrenheit readings, multiply the Centigrade reading by 1.8, and add 32 degrees.

To convert Fahrenheit readings into the corresponding Centigrade readings, subtract 32 degrees from the observed Fahrenheit reading and divide by 1.8.

TABLE 3.—VAPOR TENSION OF WATER IN MILLIMETERS OF MERCURY

°C.	mm.	°C.	mm.	°C.	mm.
0	4.6	21	18.5	30	31.5
5	6.5	22	19.6	35	41.6
10	9.1	23	20.9	40	<b>54</b> .9
15	12.7	24	22.2	50	92.0
16	13.5	25	23.5	60	148.9
17	14.4	26	25.0	70	233.3
18	15.3	27	26.5	80	354.9
19	16.3	28	28.1	90	525.5
20	17.4	29	29.8	100	760.0

# TABLE 4.—TABLE OF SOLUBILITIES

S, soluble in water. A, soluble in acids, insoluble in water. P, partially soluble in water, soluble in dilute acids. I, insoluble in dilute acids and in water. a, slightly soluble in acids, insoluble in water.

					_				1		_			
	Acetates	Bromids	Carbonates	Chlorates	Chlorids	Chromates	Hydroxids	Iodids	Nitrates	Oxids	Phosphates	Silicates	Bulfates	Sulfids
Aluminum Ammonium Barium Calcium Copper Iron" Lead Magnesium Manganese Mercury' Potassium Silver Sodium Tin" Strontium	<b>8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 </b>	00000000000000000000000000000000000000	S A A A A A A A S A S A	o: 000000000000000000000000000000000000	000000000000000000000000000000000000000	SAPS SAPSASA PEASA PE	A S S P A A A A A A A A A A A A A A A A	33555555P35AA5H355555		S P A A A A A A A A A A A A A A A A A A	A A A A A A A A A A A A A A A A A A A	a	SSIASSSASSPSSPSSSAS	A S S A A A A A A A A S A S A A S
Zinc	S	S	A	S	S	S	A	B	B	A	A	A	Ö	A 

Table 5.—Solubility of Gases in Water

Volume of gas (reduced to S. T. P.) that can be dissolved in 1 volume of water.

Gas	0°C.	10°C.	20°C.
Hydrogen	0.0215	0.0195	0.0182
Nitrogen	0.0238	0.0196	0.0164
Air	0.0288	0.0226	0.0187
Oxygen	0.0490	0.0380	0.0310
Carbon dioxid	1.713	1.194	0.878
Chlorin	•••••	3.095	2.260
Hydrogen sulfid	4.686	3.520	2.672
Sulfur dioxid	79.79	56.65	39.37
Hydrogen chlorid	506.7	473.9	442.0
Ammonia	1298.9	910.4	710.6

TABLE 6.—SOLUBILITY OF SALTS

The numbers give the number of grams of anhydrous salt that can be dissolved in 100 grams of water at the given temperatures.

Salt ·	0°C.	20°C.	60°C.	100°C.
Calcium hydroxid	0.18	<u>.</u>		0.08
Calcium sulfate (gypsum)	0.24			0.222
Mercuric chlorid	4.4	6.5	14.0	54.0
Potassium sulfate	7.6	11.3	17.8	24.3
Potassium chlorate	3.5	7.5	26.0	56.0
Potassium nitrate	13.4	26.0	110.0	246.0
Copper sulfate	14.7	21.7	39.0	73.5
Sodium chlorid	35.5	36.3	37.9	39.8
Potassium chlorid	28.5	34.0	45.2	56.3
Potassium bromid	<b>54</b> .5	65.3	86.0	105.0
Sodium nitrate	73.0	88.0	125.0	176.0

TABLE 7.—PHYSICAL CONSTANTS OF IMPORTANT ELEMENTS

		Specific	weight	Melting	Boiling	
Name	Valence	Water	Air	point	point	
			1 .	degrees C.	degrees C.	
Aluminum	3	2.7		657	2200	
Antimony	3, 5	6.62		630	1600	
Arsenic	3, 5	5.73	<b> </b>	sublimes		
Barium	2	3.8	1	850	950	
Bismuth	3, 5	9.78	l	270	1435	
Boron	3	2.45		infusible	3500	
Bromin	1, 3, 5	3.1		-7.3	59	
Calcium	2	1.54		810		
Carbon	4	1.7-3.5		infusible	3600	
Chlorin	1, 3, 5, 7		2.49	-102	-33.6	
Chromium	2, 3, 6	6.9		1520	2200	
Cobalt	2, 3	8.72		1480		
Copper	1, 2	8.9	l l	1083	2310	
Fluorin	1		1.31	-223	-187	
Gold	1, 3	19.3		1063	2530	
Hydrogen	1		. 069	-259	-252	
Iodin	1, 5, 7	4.9		114	184	
Iron	2, 3	7.86	l l	1530	2450	
Lead	1, 2, 3, 4	11.34		327	1525	
Magnesium	2	1.74		650	1120	
Manganese	2, 3, 4, 6, 7	7.4		1260	1900	
Mercury	1, 2	13.56		-38.8	357	
Nickel	2, 3	8.7		. 1450		
Nitrogen	1, 2, 3, 4, 5		0.96	-213	-195	
Oxygen	2		1.10	-218	-182	
Phosphorus	3, 5	1.8-2.3		44.1	290	
Platinum	4	21.4		1755		
Potassium	1	0.87		62.5	757	
Radium	2					
Silicon	4	2.4		1420	3500	
Silver	1	10.5		961	1952	
Sodium	1	0.97		97.6	877	
Strontium	2	2.5		900		
Sulfur	2, 4, 6	2.0		114.5	444.6	
Tin	2, 4	7.0-7.3		232	2200	
Tungsten	6	18.7		3000		
Zinc	2	7.1		419	918	
<b>21110</b>	~			410	010	

Table 8.—Heat of Formation of Compounds

The numbers show the number of large calories of heat liberated during the formation of one mole of the compound. The minus sign indicates that heat is absorbed during the formation of the compound.

Name of compound	Symbol	Heat of formation	
Hydrogen oxid (water)	H <sub>2</sub> O	68.8	
Hydrogen peroxid	H <sub>2</sub> O <sub>3</sub>	45.2	
Hydrogen chlorid	HCl	22.0	
Hydrogen bromid		8.4	
Hydrogen iodid		-6.1	
Hydrogen fluorid		37.6	
Hydrogen nitrid (ammonia)	H <sub>8</sub> N	12.0	
Hydrogen sulfid	H <sub>2</sub> S	4.8	
Nitric acid		41.6	
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	192.9	
Sodium hydroxid	NaOH	102.0	
Potassium hydroxid	КОН	104.6	
Sulfur dioxid		71.0	
Carbon dioxid	CO <sub>2</sub>	97.0	
Carbon monoxid	CO	25.7	
Phosphorus pentoxid	P <sub>2</sub> O <sub>5</sub>	369.7	
Magnesium oxid	MgO	146.0	
Calcium oxid	CaO	131.5	
Zinc oxid	ZnO	86.0	
Cupric oxid	CuO	<b>37.2</b>	
Mercuric oxid	HgO	21.5	
Ferric oxid	Fe <sub>2</sub> O <sub>3</sub>	195.6	
Magnetic iron oxid	Fe <sub>8</sub> O <sub>4</sub>	268.0	
Silver oxid	Ag <sub>2</sub> O	7.0	
Aluminum oxid	Al <sub>2</sub> O <sub>3</sub>	392.6	
Sodium sulfate	Na <sub>2</sub> SO <sub>4</sub>	328.1	
Potassium sulfate	K <sub>2</sub> SO <sub>4</sub>	344.3	
Sodium chlorid	NaCl	97.9	
Potassium chlorid	KCl	105.7	

TABLE 9.—Composition of Alloys

	Name	Composition
Aluminum	Magnalium	Aluminum, 90-98 per cent.; magnesium, 2-10 per cent.
	Aluminum copper	Aluminum, 95-97 per cent.; copper, 3-5 per cent.
Bismuth	Wood's metal	Bismuth, 50 per cent.; lead, 25 per cent.; tin, 12.5 per cent.; cadmium, 12.5 per cent.
	Rose's metal	Bismuth, 82 per cent.; lead, 9 per cent.; tin, 9 per cent. Bismuth, 50 per cent.; lead, 25 per cent.; tin, 25 per cent.
Copper	Brass	Copper, 60-80 per cent.; sinc, 20-40 per cent.; lead, 0.1 per cent.
	Bronse	Copper, 92 per cent.; tin, 8 per cent.
	Gun metal	Copper, 90 per cent.; tin, 10 per cent.
	Bell metal	Copper, 75 per cent.; tin, 25 per cent.
	Copper coins	Copper, 95 per cent.; tin, 4 per cent.; sinc, 1 per cent.
	Nickel coins	Copper, 75 per cent.; nickel, 25 per cent.
	Aluminum bronse German silver	Copper, 90-98 per cent.; aluminum, 2-10 per cent. Copper, 50 per cent.; nickel, 25 per cent.; sinc, 25 per cent.
Gold	U. S. coins	Gold, 90 per cent.; copper, 10 per cent.
	18-karat gold	Gold, 75 per cent.; copper, 25 per cent.
	14-karat gold 10-karat gold	Gold, 58.3 per cent.; copper, 41.7 per cent. Gold, 41.6 per cent.; copper, 58.4 per cent.
Iron	Steel	Iron, 99.8-98 per cent.; carbon, 0.2-2 per cent.
	Nickel steel	Iron, 94 per cent.; nickel, 5 per cent.; carbon, 1 per cent.
	Chromium steel	Iron, 95-97 per cent.; chromium, 2-4 per cent.; carbon, 1 per cent.
	Manganese steel	Iron, 92 per cent.; manganese, 7 per cent.; carbon, 1 per cent.
	Tungsten steel	Iron, 91-92 per cent.; tungsten, 7-8 per cent.; carbon, 1 per cent.
	Molybdenum steel	Iron, 94.5-96 per cent.; molybdenum, 3-4 per cent.; carbon, 1-1.5 per cent.
Lead	Solder	Lead, 33-66 per cent.; tin, 33-66 per cent.
	Pewter	Lead, 18-75 per cent.; tin, 25-82 per cent.
	Type metal	Lead, 80 per cent.; tin, 5 per cent.; antimony, 15 per cent.

TABLE 9.—Composition of Alloys—(Continued)

	Name	Composition
Mercury	Tin amalgam Silver amalgam Copper amalgam	Tin and mercury, variable proportions. Silver and mercury, variable proportions. Copper and mercury, variable proportions.
Silver	U. S. coins Sterling	Silver, 90 per cent.; copper, 10 per cent. Silver, 92.5 per cent.; copper, 7.5 per cent.
Tin	Britannia Babbitt	Tin, 85 per cent.; antimony, 10 per cent.; copper, 2 per cent.; sinc, 3 per cent. Tin, 45.5 per cent.; lead, 40 per cent.; antimony, 13 per cent.; copper, 1.5 per cent.

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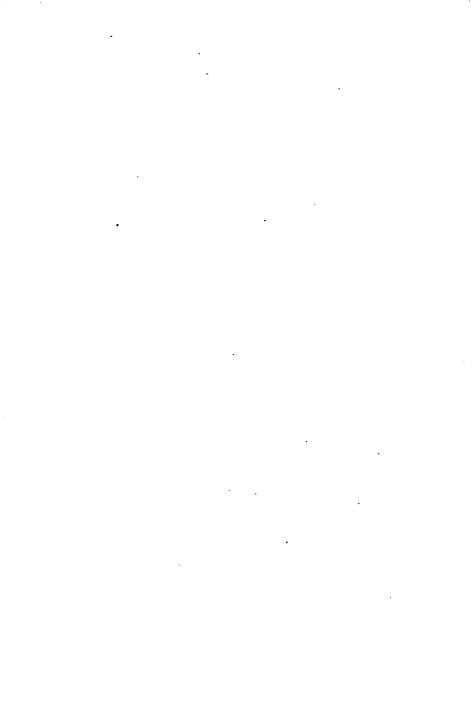
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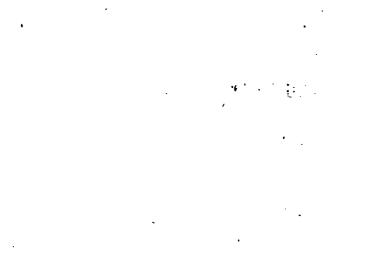




LIST OF ELEMENTS, THEIR SYMBOLS AND ATOMIC WEIGHTS. (O = 16.)

The more important elements are printed in heavy type.

Name of element	Symbol	Atomic weight	Name of element	Symbol	Atomic weight
Aluminum	Al	27.1	Molybdenum	Мо	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba.	137.37	Niton	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	<u>B</u>	11.0	Osmium	Os	190.9
Bromin	Br	79.92	Oxygen	0	16.00
Cadmium	Cd	112.4	Palladium	Pd	106.7
Caesium	C <sub>8</sub>	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	<b>195.2</b>
Carbon	C	12.00	Potassium	K	39.1
Cerium	Ce	140.25	Praseodymium .	Pr	140.6
Chlorin	Cl	35.46	Radium	Ra	226.4
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	· Ço	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa.	150.4
Dysprosium	Dу	162.5	Scandium	Ss	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	<u>E</u> u	152.0	Silicon	Si	28.3
Fluorin	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na.	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulfur	8	32.07
Glucinum	Gl	9.1	Tantalum	Ta.	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008		Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodin	I	126.92	Tin	Sn	119.0
Iridium	<u>I</u> r	193.1	Titanium	Ti	48.1
<u>Iron</u>	Fe	55.84	Tungsten	<b>W</b>	184.0
Krypton	Kr	82.92	Uranium	U	238.5
Lanthanum		139.0	Vanadium	V	51.0
Lead	Pb	207.1	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium	Yb	172.0
Lutecium	Lu	174.0	Yttrium	Yt	89.0
Magnesium		24.32	Zinc	Zn	65.37
Manganese		54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6	1		l



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